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PREFACE

We thank the authors of this volume who have provided us with an up-to-date account of recent progress in a substantial portion of the fields of physical chemistry. Again, most of the chapters review fields which are covered regularly, with about the usual number of new or occasionally-reported areas. We are fortunate not only in the competence of our authors, but in their wide geographical distribution both in this country and abroad. This aids in the eventual coverage of all shades of opinion.

The assistant editors, Miss Lois Cox and Mrs. Jean Armstrong, together with our printer, the George Banta Company Inc., have been particularly effective in transmitting the chapters of manuscript into a book. Our subject index has been prepared by Miss Lois Durham. The Cumulative Title Index will facilitate reference to earlier reviews.

Finally, we welcome any suggestions for making this review of physical chemistry increasingly effective.

J.B.	D.F.H.
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PHYSICAL ORGANIC CHEMISTRY¹

BY A. N. BOURNS AND ERWIN BUNCEL

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Because of space limitations the authors found it necessary to restrict the scope of this review. Notable among omitted topics is the chemistry of free radical processes, a subject that received a comprehensive treatment from Hine in last year's review. Particular emphasis is given to isotope effects, partly because of important recent developments in theory and application, and partly because of the reviewers' special interest in this field.

Among recent books of interest to physical organic chemists are those by Ginsburg (1), Melander (2), Olah (3), Pauling (4), Wheland (5), and Williams (6). The following topics, not specifically treated in this article, have been reviewed elsewhere during the year: benzylic acid and related rearrangements (7), substitution reactions at the bridgehead of bicyclic compounds (8), carbenes (9), hydride-transfer reactions (10), and conformational effects (11, 12).

ISOTOPE EFFECTS

Primary kinetic isotope effects.—Kinetic isotope effect studies provide one of the most useful and direct methods for obtaining information concerning the transition state (2, 13). With relatively few exceptions such studies have been restricted to reactions involving a bond to hydrogen, since only with the isotopes of this element are rate differences sufficiently large to permit measurement by ordinary kinetic methods or by simple isotopic assay techniques. The isotope effects associated with other elements, however, in particular carbon, nitrogen, oxygen, and sulfur, may be evaluated with precision limits not greatly exceeding those usually associated with hydrogen isotope effects, e.g., a nitrogen isotope effect k_{14}/k_{15} of 1.020 to within less than ± 0.001 (14). Although more elaborate techniques are required, time-consuming isotopic labelling may be avoided by using compounds of natural isotopic abundance.

An important problem in the theoretical evaluation of a kinetic isotope effect is the calculation of the high temperature limit (temperature-independent term) of the effect. Two approaches, the Slater and the Eyring, have been considered in the past and, although they lead to the same result when applied to the dissociation of a diatomic molecule, they do not necessarily do so with more complex systems. Wolfsberg (15) has discussed this problem in relation to the rupture of the A—B bond in the molecule R—A—B—R'. If the R—A and B—R' bonds simultaneously shorten as the AB bond is lengthened, then the Slater method may be used and the high temperature limit becomes $(\mu_2/\mu_1)^{1/2}$, where the μ 's refer to the reduced

¹ The survey of literature pertaining to this review was concluded December 1, 1960.

masses of isotopic diatomic AB molecules. If, however, the force constant of the A—B bond is much smaller than that of the other bonds, the normal mode of decomposition will be one that takes apart the centers of mass of the RA and R'B fragments. In this case, the high temperature limit will be given by the square root of the ratio of the reduced masses of the isotopic RA—BR' molecules (i.e., $\mu = M_{RA}M_{R'B}/M_{RA} + M_{R'B}$).

In a continuation of their extensive studies on the C¹³ isotope effect in malonic acid decarboxylation, Yankwich *et al.* (16) have found that in quinoline solution both the intramolecular and intermolecular isotope effects are about 1 per cent higher than the corresponding effects in dioxane. This additional effect is ascribed wholly to an equilibrium effect associated with the formation of a quinoline-malonic acid complex. Incompatible with theory is their observation that at temperatures below 100°C. the intramolecular effect becomes significantly larger than the intermolecular effect. Stothers & Bourns (17) have found that both ethanolysis and methanolysis of 1-bromo-1-phenylethane give rise to the very small carbon isotope effect, k_{12}/k_{13} , of 1.006, a result requiring that both the temperature-independent and free-energy components of the effect be small. The small temperature-independent term supports the mass fragment method, which would appear to be appropriate here since the force constant of the bond being ruptured is relatively small, while the small free-energy term suggests that conjugation of the isotopic carbon with the ring in the transition state leading to carbonium ion compensates largely for the loss of the carbon-bromine vibration. Lynn & Yankwich (18) have found that the reaction of cyanide ion with methyl iodide gives rise to an isotope effect, k_{12}/k_{13} , of 1.015 with respect to the reagent, and of 1.074 with respect to the organic halide; Riesz & Bigeleisen (19) have observed only a very small solvent effect on the C¹³ isotope effect in the decarboxylation of trinitrobenzoate ion.

Brodskii *et al.* (20) have reported the surprising result that in the high-temperature cracking of ethane to methane the rate of rupture of a C¹⁴—C¹⁴ bond is actually faster than that of a C¹²—C¹⁴ bond. The theoretical basis for their hypothesis that the enhanced rate of the heavier isotopic molecule has its origin in the extra plane of symmetry of this species is not immediately apparent.

A striking demonstration of the effect of quantum-mechanical tunnelling in proton-transfer reactions has been provided by Hulett (21). Using equations developed by Bell (22) it was estimated that, largely as a result of tunnelling, the isotope effect k_H/k_D in the fluoride-ion-catalyzed bromination of 2-carbethoxycyclopentanone should increase from the 2.7 observed at 25°C. to the very large value of 16 at -20°C. The observed effect at this temperature has been found to be greater than 10, in confirmation of this prediction.

The danger inherent in calculating an isotope effect from the difference in isotopic content of the reactant and the product in a system in which the reaction being investigated is accompanied by side reactions has been very

effectively demonstrated by Eliel *et al.* (23). In the arylation of benzene- d and of benzene—benzene- d_6 mixtures, the isotope effect k_H/k_D based on the deuterium content of the diaryl product is greater than unity, whereas the isotopic composition of the benzene—benzene- d_6 mixture remains unchanged during reaction. These seemingly contradictory results are accounted for on the basis of isotopically discriminating, competitive reactions involving the arylcyclohexadienyl intermediate formed in the initial slow step.

A number of recent applications of kinetic isotope effects in reaction mechanism investigations are cited in other sections of this review.

Solvent isotope effects.—The effect upon reaction rates and equilibrium constants of a change in solvent from H_2O to D_2O , i.e., the solvent isotope effect, has been receiving renewed attention. Although the effect continues to be used as a criterion of mechanism in acid- and base-catalyzed reactions, its limitations in this respect have been delineated in recent theoretical studies. Solvent isotope effects in a number of solvolytic processes, not involving proton transfer, have been measured and have contributed to our understanding of the structure of water and the effect of charged and uncharged species on this structure.

Swain *et al.* (24, 25) have calculated the isotope effects for ionic hydration equilibria from infrared spectral data, using a structural model for water in which each molecule is tetrahedrally bonded to four other molecules and a model for an ion in solution in which the ion replaces a water molecule in its tetrahedral cell. The assumption is made that all of the thermodynamic differences for ionic solution in light and heavy water arise from differences in the frequencies for librational motion (hindered rotation) of the coordinated water molecules. Calculations have been extended to solutions of ions in mixtures of light and heavy water and excellent agreement between the observed and experimental properties has been obtained.

Laughton & Robertson (26) have now reported solvent isotope effects for the hydrolysis of alkyl halides. They propose that the major factor determining the k_{H_2O}/k_{D_2O} ratio is the relative stability of the initial state solvation shell. Neutral solute molecules, such as alkyl halides, which do not interact strongly with the solvation shell, can be expected to cause an increase in the structural difference between light and heavy water in the initial state compared to that of the pure waters. The formation of the quasi-ionic transition state will tend to decrease this difference and the reaction, therefore, will exhibit an enhanced rate in light water. It is suggested that when the solute contains polar groups that can interact with water the structural difference in the initial state will be less and a smaller k_{H_2O}/k_{D_2O} ratio will result. Thus, alkyl halides are found to give isotope effects of 1.2 to 1.4, while sulfonic esters give 1.06 to 1.09. On the other hand, relatively large effects k_{H_2O}/k_{D_2O} have been observed (27, 28, 29) in the "spontaneous" (non-catalytic) hydrolysis in water and aqueous dioxane of a wide variety of anhydrides (1.7 to 3.9), benzoyl and mesitoyl chlorides (1.5 to 1.9), methyl trifluoroacetate (1.8), *p*-methoxybenzhydryl acetate (1.9), and β -propiolactone (1.2). Since these

compounds vary widely in type and are solvolyzed by both uni- and bimolecular mechanisms, the effects are unlikely to arise from any sort of proton transfer mechanism (27). All contain polar groups, however, and, on the basis of Laughton & Robertson's proposals, might have been expected to give rise to smaller effects than do the alkyl halides. Clearly, additional work is required on this very interesting problem.

On the basis of relative ionization constants of maleic acid, bimaleate ion, and ethyl hydrogen maleate in light and heavy water, Dahlgren & Long (30) have concluded that there is less internal hydrogen bonding for deuterio bimaleate ion in deuterium oxide than for hydrogen bimaleate in water. This is opposite to what would be expected from zero-point energy considerations for gaseous molecules and the authors propose that the reversal may be the consequence of a greater hydrogen bonding of solvent deuterium oxide as compared to that of water.

Long & Bigeleisen (31), making use of partition function ratios for deuterio and protio species, have given a theoretical analysis of the relative rates in D_2O and H_2O for acid- and base-catalyzed reactions proceeding by different mechanisms. In general, reactions involving pre-equilibrium proton transfer will proceed more rapidly in D_2O , unless the proton removed in the slow step has exchanged with solvent or the catalysis is by a weak acid. In the latter cases, the reaction may be slower in heavy water. Reactions proceeding by an initial slow proton transfer from hydronium ion to substrate can be expected to be slower in D_2O , although Gold (32) has suggested that the reverse will be the case if there is a tighter bonding of the transferred hydrogen in the transition state $S \cdots H \cdots OH_2^+$ than in H_3O^+ . Willi (33), however, using the methods of statistical thermodynamics, has shown that the lower limit of k_{H_2O}/k_{D_2O} to be expected for slow proton transfer from hydronium ion is 1.7 at 25°C. It therefore would appear that the observation of $k_{H_2O} < k_{D_2O}$ can be taken as definite evidence for the pre-equilibrium proton transfer mechanism.

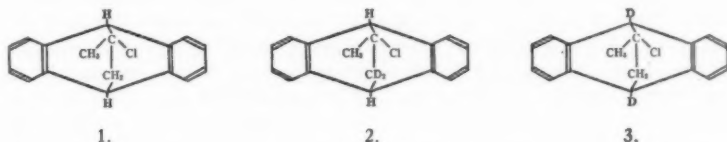
Recent calculations by Gold (32) indicate that the dependence of the rate of an acid-catalyzed reaction on the composition of light and heavy water mixtures (Gross-Butler theory) cannot be used to distinguish between pre-equilibrium proton transfers and rate-controlling proton transfers from hydronium ion to substrate. His calculations, however, have been limited to the case $k_{H_2O}/k_{D_2O} = 0.5$, a situation that is not likely to obtain for slow proton transfer (*vide supra*).

Secondary isotope effects.—The term "secondary isotope effect" is used with reference to the effect on reaction rates and equilibria of isotopic substitution at positions not directly involved in bond formation or bond rupture processes. Kinetic secondary isotope effects, in particular, have been the subject of intensive investigation during the past several years and would appear now to have attained the status of a mechanistic criterion. Recent calculations by Wolfsberg (34) have shown that sizeable effects of this kind can be

expected only if the force constants involving the isotopically substituted atoms differ considerably in the transition state from those in the reactant. This assumption is implicit in the current interpretation of secondary isotope effects in terms of zero point energy changes (*vide infra*).

Kinetic secondary hydrogen isotope effects were first observed in solvolytic reactions and were associated with isotopic substitution of β -hydrogen atoms. The most recent contribution in this field was made by Robertson *et al.* (35) who measured the β -deuterium effects in water solvolysis of ethyl, isopropyl, and *t*-butyl sulfonates and halides. Their results confirmed the earlier findings of Lewis (36) and of Shiner (37) that the greater the electron deficiency at the reaction center the greater the magnitude of the effect k_H/k_D .

An impressive body of evidence based on structural and stereochemical data has accumulated in support of the interpretation of β -deuterium effects in terms of bond weakening of the C—H and C—D bonds in the transition state because of hyperconjugative electron release to the electron-deficient reaction center (36, 37). A striking demonstration of the importance of this factor has been provided by Shiner (38) who compared the relative solvolysis rates of Compounds 1, 2, and 3.



Whereas a normal isotope effect, $k_H/k_D = 1.14$, is found for structures 1 and 2, a very small "inverse" effect, $k_H/k_D = 0.99$, is observed for structures 1 and 3. In the latter case, the hyperconjugative effect cannot operate since the two orbitals that must overlap are mutually perpendicular. Additional evidence supporting hyperconjugative effects is found in the effect of deuterium substitution both on the rate of alkaline hydrolysis of ethyl acetate and on the equilibrium between ketones and hemiketals (39).

Bartell (40) and Robertson *et al.* (35) have proposed, independently and from a somewhat different point of view, that non-bonding interactions ("intramolecular van der Waals forces") may be an important source of the β -deuterium isotope effect. These forces will be weaker in the less crowded trigonal transition state and therefore will make a smaller contribution to the zero-point energy sum; thus reaction of the undeuterated compound will be favoured. It has been suggested (35) that the marked drop in the isotope effect resulting from the introduction of a *p*-phenylene group between the isotopically substituted group and the reaction center may be caused, in part, by the elimination of this repulsive energy factor. On the other hand, an experiment designed to test the hypothesis failed to detect a

difference in the non-bonding interaction between CH_3 and CD_3 in a Meerwein-Ponndorf-Verley reduction involving isopropanol (41).

Halevi (42) has suggested that a cause of secondary isotope effects in acid-base dissociation processes, and possibly in rate processes, is to be found in differences in the molecular dimensions (bond length and angle) of isotopic molecules arising from anharmonicity. In attempting to determine whether such differences might account for β -deuterium effects in solvolytic reactions, Halevi *et al.* (43) have calculated, by the LCAO-MO method, the effect of deuteration in the methyl group on the stability of the ethyl carbonium ion. The results are inconclusive, but they at least suggest that a hyperconjugative destabilization of the deuterated, relative to normal, carbonium ion could possibly outweigh an inductive stabilization favouring the deuterated species, and hence account for the direction of observed β -deuterium isotope effects.

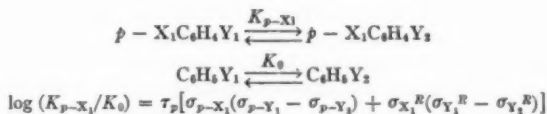
When deuterium is substituted for hydrogen on an α -carbon atom, the isotope effect $k_{\text{H}}/k_{\text{D}}$ in nucleophilic substitution ($\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$) reactions may be either greater or less than unity. Recent studies by Robertson *et al.* (44, 45) have substantiated earlier suggestions (46) predicting an inverse relationship between the magnitude of the isotope effect $k_{\text{H}}/k_{\text{D}}$ and the degree of participation of the nucleophile in the transition state. Reactions of the "limiting" type give $k_{\text{H}}/k_{\text{D}}$ ratios greater than unity, and this has been attributed (46) to a change in hybridization from sp^3 to sp^2 , resulting in a change in zero-point energy in the direction that will favour the reaction of the lighter reactant. Robertson *et al.* (45) have pointed out, however, that there is insufficient evidence to show that the change in hybridization will necessarily cause a zero-point energy decrease in the transition state. They have suggested that non-bonding, repulsive energy changes (*vide supra*), which in "limiting" reactions will inevitably operate in the direction favouring the lighter reactant, may contribute in an important way to the isotope effect. α -Isotope effects of less than unity have been attributed (44, 45, 46) to a stiffening of the out-of-plane vibrational frequency of the C—H bond in the transition state as a consequence of crowding resulting from the close proximity of both nucleophile and leaving group.

Surprisingly large inverse γ -deuterium isotope effects $k_{\text{H}}/k_{\text{D}}$ ranging from 0.92 to 0.95 have been observed for solvolysis in water of *n*-propyl halides and sulfonates (47). These have been attributed to hindered vibration of the γ - CH_3 group in a transition state of *gauche* conformation which places this group and the leaving group in spatial conflict.

STRUCTURAL AND MEDIUM EFFECTS ON RATES AND EQUILIBRIA

Linear free energy relationships.—Hine (48) has developed a Hammett-type equation based on the assumption that substituents add two quantities to the total free energy content of a molecule or ion, one of which is proportional to the product of their so-called polar substituent constants while the other is proportional to the product of their resonance substituent constants.

For an equilibrium involving *para* substituents, we have the following equation:



where K_{p-X_1} and K_0 are equilibrium constants, τ_p is a proportionality constant describing the efficiency of *para* interactions of substituents under the particular reaction conditions, the σ_p 's are polar substituent constants which are characteristic of the polar interaction of the substituents with other substituents *para* to them, and the σ^R 's are resonance substituent constants whose products are defined as zero if they are of the same sign (no resonance interaction). For processes involving *meta* substituents a similar equation is derived except that the resonance interaction is considered to be zero. By means of these equations, $\log K/K_0$ values for four different reaction series, the ionization of benzoic acids, phenols, and anilinium ions, and the solvolysis of *t*-cumyl chloride, have been correlated with a high degree of precision.

It is well known that no single set of σ values can successfully correlate rates for different reaction series, even of the same reactivity type, if the electrical demand at the reaction center varies over wide limits from reaction to reaction (49). This is particularly so for *para* substituents in reactions of the electrophilic type. Yukawa *et al.* (50, 51) have now derived the following equation which gives an excellent correlation of rates for a wide variety of electrophilic reactions:

$$\log k/k_0 = \rho(\sigma + r\Delta\sigma_R^+),$$

where σ is the Hammett substituent constant, r is a constant which provides a measure of the resonance demand of the positive reaction center, $\Delta\sigma_R^+$ is equal $\sigma^+ - \sigma$, where σ^+ is the Brown & Okamoto (52) substituent constant derived from *t*-cumyl chloride solvolyses, and ρ , the reaction constant, is identified with ρ_m or is calculated by solving the above regression equation. Whereas Brown and Okamoto's equation, $\log k/k_0 = \rho\sigma^+$, can be used successfully for reactions having r values within 0.7 to 1.3, this new expression gives a satisfactory fit for reactions with r ranging from 0.2 to 2.3.

Using substituted amines as a standard, Kaufman & Koski (53) have developed a new set of substituent constants δ_K that provide a quantitative measure of the change in ionization potential of a molecule or radical with substitution. These constants, which have both polar and resonance components, are additive, and it is suggested that they provide a measure of the "absolute" Lewis base strength of a molecule uncomplicated by steric factors.

Hyperconjugation.—It has been suggested by several workers in recent years that the Baker-Nathan order of reactivity (hyperconjugation) is caused entirely or in part by solvent effects. Schubert *et al.* (54, 55) have ascribed the order to steric hindrance of solvation of the transition state at

electron-deficient sites near the alkyl substituent, whereas Shiner (56) has suggested that the role of solvent may be to enhance C—H over C—C hyperconjugation. Clement *et al.* (57) have now examined differential solvation effects for the ground state in the solvolysis reactions of *p*-methylbenzyl and *p*-*t*-butylbenzyl chlorides in methanol and have concluded that these effects are of sufficient magnitude to obscure completely any inherent structural effects. This perhaps is not unexpected in the reaction systems chosen since the difference in free energy of activation of the two compounds is only 68 cal./mole. Unfortunately, the test, of necessity, requires an assumption concerning the magnitude of differential solvent effects for the transition states that may or may not be valid. Nevertheless, its extension to systems with larger free energy of activation differences would be of considerable interest.

Benkeser *et al.* (58) have found support for the proposal that solvation effects are responsible for the Baker-Nathan order in the observation that mercuridesilylation of aryltrimethylsilanes in glacial acetic acid gave the rate order $\text{CH}_3 < \text{CH}_3\text{CH}_2 < (\text{CH}_3)_2\text{CH} < (\text{CH}_3)_3\text{C}$, whereas protodesilylation in the more polar aqueous acetic acid gave the expected rate sequence. On the other hand, the chemical shifts found for the alkylbenzenes in the nuclear magnetic resonance studies indicate that the Nathan-Baker order holds even in a non-polar solvent such as cyclohexane (59).

Studies of the substituent and solvent effects on the $n \rightarrow \pi^*$ transition in aliphatic carbonyl and nitro compounds have provided evidence for hyperconjugation in the electronically excited states of molecules (60, 61).

Medium effects.—The importance of differential solvation effects in determining the magnitude of the activation parameters in solvolytic reactions of neutral solutes has long been recognized, although attention has been focussed mainly on the degree of solvation of the quasi-ionic transition state. Drawing from his extensive data for solvolysis in water, Robertson (62) has presented convincing arguments in support of the hypothesis that the stability of the initial state solvation shell makes an important contribution to the activation process. Thus, the higher entropy of activation for hydrolysis of *i*-propyl bromide compared to methyl bromide is in the opposite direction to that predicted on the basis of a more ionic transition state, but it can be readily understood in terms of a higher degree of structure associated with the initial state solvation shell.

An interesting explanation has been given by Hyne (63) for the variation in activation energy with solvent composition often found for solvolytic reactions in binary solvent mixtures. An activation energy maximum is observed in alcohol-water mixtures for reactions of the type $\text{ion} \rightarrow \text{dipole}$ (solvolysis of onium salts), and an activation energy minimum for reactions of the reverse type, $\text{dipole} \rightarrow \text{ion}$ (solvolysis of halides). The order of increasing depth of the minima has been found to parallel the order of increasing sensitivity of reaction rate to the ionizing power of the medium. It is suggested that these phenomena are a consequence of the greater selectivity of an ionic species, reactant or transition state, for the more polar component of the medium.

This interpretation is in contrast to Laidler's (64) treatment of solvent effects based on electrostatic theory, in which a continuous medium of uniform dielectric constant is assumed.

Grunwald *et al.* (65) have studied the kinetic salt effects in the solvolysis of neophyl tosylate and in the racemization of L-(+)-*threo*-3-phenyl-2-butyl tosylate in 50 per cent dioxane-water and have shown that these effects are highly specific and are associated with the ionization step. Values of the parameter S in the equation $\log k/k_0 = Sm$, where m is the salt molality, range from 0.5 for NaClO_4 to -0.6 for NaOH . These results are interpreted on the basis of the effect of salts on the activity coefficients of non-electrolytes (66). The variation in S with inorganic salts is then ascribed to long-range electrostatic and salt-induced medium effects; while with organic salts, short-range interaction between organic ions and organic non-electrolytes is indicated.

Evidence that an increase in the ionizing power of the solvent causes an increase both in the contribution to the resonance hybrid of dipolar resonance structures (67), $^+X=C_6H_4=Y-O^-$, and in the degree of electron release from alkyl groups in alkyl benzenes (59) has been provided by nuclear magnetic resonance measurements.

ACIDITY FUNCTIONS AND THEIR APPLICATION

The unified (solvent independent) acidity scale $pA = -\log a_+ = pH - \log f_H$ (a_+ is the proton activity, f_H is the degenerate activity coefficient, and $pH = -\log a_{\text{lyonium ion}}$), evaluated by Grunwald (68) for the system ethanol-water, has been extended by Izmailov (69) to methanol-water mixtures, several aliphatic alcohols, formic acid, and ammonia. The pA values of solutions of acids and bases (not exceeding 1 M) in these solvents cover the following ranges: ethanol, -4.2 to $+15.1$; methanol, -3.3 to $+13.5$; formic acid, -8.6 to -2.5 ; and ammonia, $+16.4$ to $+49.1$.

Several new measurements on acidity functions have been reported. Högfeldt & Bigeleisen (70) have determined D_0 for DCl solutions (10^{-4} –1 M) and D_2SO_4 solutions (10^{-4} –12 M) in D_2O and have redetermined H_0 for corresponding solutions in H_2O . It is found that $D_0 = H_0$, except in 10^{-3} to $10^{-1} M$ sulfuric acid, where the slight difference is due to DSO_4^- being a weaker acid than HSO_4^- . For the indicator bases examined pK_{BD^+} is greater than pK_{BH^+} by 0.3 to 0.6 units. The H_0 scale has been evaluated for the formic-acid-water system (71) and further measurements have been reported for nitric acid solutions (72). The H_- function has now been extended (73) to the value 20, which is obtained for an aqueous 95 mole per cent tetramethylene sulfone solution of phenyltrimethylammonium hydroxide. Solvation of hydroxide ion by four molecules of water is indicated. The $H_R(J_0)$ function² has been determined for perchloric acid (0.01–4.0 M) in aqueous dioxan solutions (74) and for the formic-acid-water system (71).

² Both these terms continue to be widely used to denote this acidity function whereas the term C_6 now appears to have been dropped. In this review, the symbol H_R will be employed.

In general, the experimental function H_R is found to deviate widely from the values calculated by the relationship $H_R = H_0 + \log a_{H_2O}$ (71). Taft (75) has proposed that this deviation can be accounted for not, as previously supposed, by ascribing a unique activity coefficient behaviour to the cation R^+ , but rather on the basis of an "abnormal" solvation of Hammett indicator bases. Thus, the two indicators, 2,4-dichloro-6-nitroaniline and *p*-nitrodiphenylamine, originally used by Hammett to evaluate H_0 in the region 44 to 64 per cent sulfuric acid actually give a measurable difference in H_0 , whereas H_R values measured in this region by seven arylmethanols show no such variation. Plots of $H_R - H_0$ vs. $\log a_{H_2O}$ are linear, with a slope of four for the primary amine and three for the secondary amine. This observation is consistent with hydration of the amines through hydrogen-bonding by three and two molecules of water, respectively.

Much recent work has been concerned with the use of the Zucker-Hammett hypothesis as a criterion of mechanism of acid-catalyzed reactions. A number of exceptions have been found, and alternative criteria have been proposed.

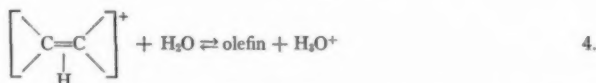
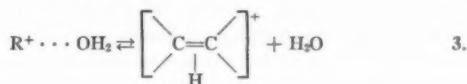
A novel interpretation of the kinetics of acid-catalyzed reactions has been proposed by Bunnett (76, 77). Plots of $\log k + H_0$ vs. $\log a_{H_2O}$ are shown to be linear for a large number of reactions. The slopes w range in value between -3 and $+8$ and are interpreted on the basis that the transition state of the rate-determining step may contain several molecules of water. The magnitude of w depends on the chemical function of water in this transition state and is indicative of the reaction mechanism. This interpretation cannot be reconciled with the Zucker-Hammett hypothesis, which seeks to differentiate between reactions having one and no molecules of water in the transition state.

Kwart (78) has applied his kinetic criterion of mechanism (79), based on the correlation of rate and indicator measurements in mixed solvents with hydrogen ion activity (68), to the acid-catalyzed ring opening of epichlorohydrin in ethanol-water mixtures and has concluded that the reaction proceeds by the A-2 mechanism. This is in contradiction to the mechanism proposed on the basis of H_0 dependence (80). Another criterion, which has led to conclusions that contradict those obtained by applying the Zucker-Hammett hypothesis, is the volume of activation derived from high pressure studies (81, 82). The criticism of the Zucker-Hammett hypothesis by Archer & Bell (83), however, is unfounded. They have observed a correlation of $\log k$ with H_0 for the enolization of acetone over the range 1 to 8 *M* HCl, when a correction is made for the protonation of acetone using the abnormally large pK of -1.58 (84). New measurements (85) give the value -7.2 for the pK of acetone, from which it follows that acetone is insignificantly protonated by 1 to 8 *M* acid and that the rate actually correlates more satisfactorily with the hydrogen ion concentration, as is to be expected for a reaction known to contain a water molecule in the transition state of the rate-determining step.

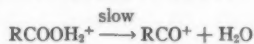
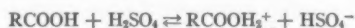
The hydrolyses of acetic and acetic-benzoic anhydrides in aqueous

dioxane are H_0 dependent but by other criteria are shown to be A-2 reactions (86). It has been proposed that in these and in related hydrolyses there is a varying degree of binding of the water molecule in the transition state, depending on the substrate, and that this leads to a continuous variation between H_0 and $\log [H_3O^+]$ dependence of rate.

New work on the alcohol-olefin conversion necessitates a revision of the Taft mechanism (87). Roček (88) and Taft *et al.* (89) have observed that the dehydration of *t*-alcohols follows the H_0 function, whereas the previous mechanism, involving rate-determining isomerization of a "free" carbonium ion to a π -complex, would require correlation with H_R . The mechanism favoured (89) to account for this discrepancy involves rate-determining isomerization of an intermediate "encumbered carbonium ion" $R^+ \cdots OH_2$ to a π -complex (step 3). Oxygen-18 exchange, which is faster than dehydration and also follows H_0 , is considered to proceed by the same mechanism, with step 2 rate-determining.



Ropp (90) has shown that the mechanism proposed by Deno & Taft (91) for the decarbonylation of triphenylacetic acid in strong sulfuric acid, which was based on a correlation of rate with H_R , is invalid. Both the absence of a measurable isotope effect in the reaction of triphenylacetic acid-2- C^{14} , and the relatively small amount of O^{18} enrichment in the carbon monoxide formed when the reaction is carried out in O^{18} enriched solvent, exclude the formation of $(C_6H_5)_2CCO^+$ in a pre-equilibrium step. Evidence is presented in support of a common mechanism for the decarbonylation of formic acid and triphenylacetic acid in strongly acid solutions:



This illustrates the caution which must be taken in basing on acidity function relationships a mechanism which is not confirmed by other studies.

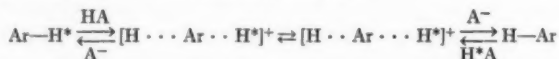
ELECTROPHILIC AROMATIC SUBSTITUTION

General theory.—In recent years a theory of electrophilic aromatic substitution has been developed (92) in which the highest occupied and lowest

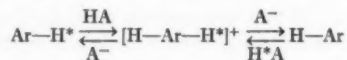
unoccupied molecular orbitals of substrate and reagent, respectively, are given a dominant role. This theory, with a related treatment for nucleophilic and radical substitution, has been termed the "frontier electron theory" and has led Fukui (93) and Brown (94) to propose two different reaction pathways for aromatic substitution, both involving charge transfer between substrate and reagent. In a recent paper (95), Fukui has compared the two approaches and has shown that, despite their common basis, they lead to two mutually contradictory conclusions concerning the relationship between reactivity and the extent of charge transfer to electrophile in the transition state.

Brown's "selectivity relationship" between partial rate factors for substitution at *m*- and *p*-positions of monosubstituted benzene derivatives has been shown (96) to hold at least as well for anisole as for toluene and *t*-butylbenzene. It would seem, therefore, that resonance contributions to the electron deficient transition state, even with the highly electron-releasing methoxy group, are not as variable as might have been expected (97). The σ^+_{p-t-Bu} and σ^+_{p-OMe} values derived from the partial rate data are in excellent agreement with values based on *t*-cumyl chloride solvolysis.

Hydrogen-isotope exchange.—Gold *et al.* (98, 99) have suggested that hydrogen-isotope exchange in aromatic compounds involves a rapid and reversible proton transfer from the catalyzing acid followed by a rate-determining rearrangement of the resulting complex:



Consistent with this A-1 mechanism is: (a) a primary hydrogen-isotope effect (99, 100, 101); (b) a faster exchange rate in D_2O than in H_2O (99, 100); (c) a variation in rate with composition in H_2O - D_2O mixtures in accord with the predictions of the Gross-Butler theory (99, 100); and (d) a linear dependence of $\log k$ on H_0 (98, 100). Although observations (a), (b), and (c) can equally well be accommodated by the A-S_E2 mechanism,



Gold (100) has maintained that observation (d) requires a rate-determining step in which the conjugate base of the catalyzing acid is not part of the transition state. Others (102, 103, 104) have questioned the significance of this latter criterion for distinguishing between A-1 and A-S_E2 reactions. There is, however, one important kinetic distinction between the two mechanisms, namely, the form of the acid catalysis. An A-1 reaction can be catalyzed by hydronium ion only (in aqueous solution), whereas an A-S_E2 reaction should show catalysis by a generalized acid. Unfortunately, under the strong mineral acid conditions usually required to bring about exchange, the difference cannot be observed. Catalysis by six Brönsted acids in dilute solution has now been found for hydrogen exchange in 1,3,5-trimethoxybenzene (105,

106) and by three Brønsted acids for exchange in the 1- and 3-positions of azulene (107). In each system, the rates are correlated by the Brønsted catalysis law giving an α value of 0.5. These results clearly rule out the A-1 mechanism for these compounds and, although a generalization to include all aromatic substrates is probably not justified, the two-step sequence, which is similar to the mechanism now accepted for most other electrophilic aromatic substitution reactions, would appear to accommodate all known features of the reaction.

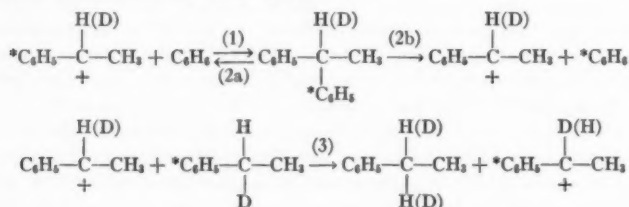
Halogenation.—Work has continued on the nature of the substituting agent in halogenations using different reagents and reaction conditions. Iodination of anisole with iodine monochloride in water shows an isotope effect, k_H/k_D , of 3.8 which persists at very low chloride ion concentration (108). This result, although in accordance with a mechanism in which H_2OI^+ is the substitution agent and proton loss is rate-determining, does not completely eliminate ICl itself as the attacking species since, even at the lowest chloride concentration used, the reverse of an ICl iodination step, forming a cationic (Wheland) intermediate and chloride ion, could still be faster than proton loss. An effect of similar magnitude has been observed (109) for iodination of anisole in glacial acetic acid under conditions in which the kinetic order with respect to ICl is two. The function of the second ICl molecule, therefore, cannot be to assist in proton removal.

Aromatic brominations show isotope effects much less commonly than iodinations. Berliner (109) has suggested that this difference may be due either to a less rapid proton loss from the Wheland intermediate that contains the less electronegative iodine, or to a more rapid return to reactants from the sterically crowded iodination complex. Support for the latter interpretation is found in the observation (110) of a tritium isotope effect, k_H/k_T , of ten in the bromination of 1,3,5-tri-*t*-butylbenzene, a reaction for which steric crowding should be severe. De la Mare *et al.* (111, 112) have furnished kinetic evidence that in chlorination by hypochlorous acid in aqueous acetic acid the active substitution agents are chlorine acetate and its protonated form $ClOAcH^+$. The unexpected observation was made that chlorine acetate is a more powerful electrophile than molecular chlorine.

Sulfonation.—Leading from the assumption that the activity coefficient ratio $f_X f_Y / f_{XY} \approx \text{constant}$ in H_2SO_4 solutions regardless of charge, Brand *et al.* (113) have accounted for the substrate isotope effect, k_H/k_D , of 1.6 to 2.0 and the solvent isotope effect, $k_{H_2SO_4}/k_{D_2SO_4}$, of 1.4 observed in aromatic sulfonation in terms of a stepwise attachment of SO_3 and H^+ to the substrate. Their interpretation requires that reactions involving the removal of a proton from the ring-carbon and from the sulfonic acid group proceed at about the same slow rate. This would seem most unlikely. The difficulty arises as a consequence of the authors' assumption that D_2SO_4 is a stronger acid than H_2SO_4 in reaction with the base $H-Ar^+-SO_3^-$. There is actually some reason to believe that the opposite is true (114).

Friedel-Crafts reactions.—An ingenious experiment by Streitwieser & Reif (115) has proved invalid the bimolecular nucleophilic displacement

mechanism (116, 117) for the transalkylation (disproportionation) reaction of ethylbenzene in the presence of hydrogen bromide and a Lewis acid. When ethylbenzene- α - d -ring- C^{14} was treated in benzene solution with $GaBr_3$ and hydrogen bromide, C^{14} activity and optical activity were progressively lost from the ethylbenzene and at approximately the same rate, whereas deuterium scrambling occurred at a slower rate. The following mechanism with step (3) rate-determining was proposed:



NUCLEOPHILIC SUBSTITUTION AT SATURATED CARBON

S_N2 and S_N1 reactions.—Recent work has emphasized the importance of considering, in nucleophilic substitution reactions, the extent of association of reactant salts in organic solvents. A lack of such data, for example, has prevented Ross *et al.* (118) from assigning a true rate constant, in the absence of salt effects, to the reaction of benzyldimethylanilinium ion with ethoxide in ethanol. Winstein *et al.* (119) have concluded that the relative reaction rates of halide salts (MCl, MBr, MI) in bimolecular substitution reactions is not necessarily a true measure of the relative nucleophilicity of dissociated halide ions, since much of the reagent may exist in the form of less reactive ion-pairs, ion-triplets, etc. They have shown that when the observed second-order rate constant for reaction in acetone is divided by the degree of dissociation of the salt, the resulting rate constants for reaction of dissociated anions are in the order $Cl^- > Br^- > I^-$. One would therefore conclude that in this solvent such factors as initial state solvation, polarizability, and intramolecular van der Waals-London cohesion forces in the transition state (120, 120a) are outweighed by factors relating to the steric requirements of the attacking ion and the energy of the C—X bond being formed. The reversed order found in water can then be attributed to a greater sensitivity to solvent change of chloride, relative to iodide ion.

Winstein *et al.* (121) have pointed out that the observation of a second-order term in the kinetic expression governing the rate of reaction of *t*-butyl halides with salts is not a valid criterion for a *S_N2* component of the reaction since ionization rates are known to increase linearly with salt concentration. *t*-Butyl bromide in the presence of amines and lithium or quaternary ammonium salts, either separately or in combination, gives isobutylene as the major reaction product both in solvent acetone (121) and in nitromethane (122). Reaction is therefore considered to proceed by an initial ionization of the organic halide, even at the high salt concentrations where the second order component becomes important. A carbonium ion mechanism is also

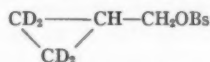
indicated for the exchange between *t*-butyl chloride and radio-chloride ion in aqueous methanol (123), and for the solvolysis of *m*-halobenzyl tosylates in aqueous acetone (124).

The reaction of diphenylmethyl bromide in nitromethane with tetraethylammonium bromide, chloride, and azide, and with a number of amines, is also governed by kinetic expressions that have both first- and second-order components, the rate constant for the former being the same in all reactions (125). Although the second-order term for the reaction with salts could be interpreted as resulting from an acceleration of ionization rate by a salt effect, no such explanation can account for this term in the reaction with amines. It seems reasonable, therefore, that in all of these reactions of diphenylmethyl bromide the first- and second-order components represent concurrent S_N1 and S_N2 processes.

The results of a careful kinetic study (126) of the reaction of silver salts with alkyl halides in acetonitrile have been interpreted on the basis of an ion-pair mechanism in which the rate-determining step involves both silver cation and its accompanying anion: $X^- + RI + Ag^+ \rightarrow X^-R^+ + AgI$. The silver ion-assisted hydrolysis of *cis*- and *trans*-crotyl chlorides has also been re-examined (127). It is shown that formation of unrearranged primary butenyl solvolysis products proceeds with preservation of configuration about the double bond, although some *cis-trans* conversion does take place via the accompanying structural isomerization. Thus a significant energy barrier exists between *cis* and *trans* allylic butenyl cations.

Non-classical carbonium ions.—This field has received considerable attention recently and a number of novel developments have been reported.

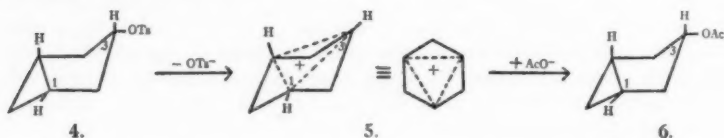
The kinetic deuterium isotope effect has been used (128) in an attempt to determine whether the product of the rate-determining step of the solvolysis of cyclopropylcarbinyl derivatives is a classical cyclopropylcarbinyl cation or a non-classical cyclobutonium cation (129). On the assumption that the formation of a cyclobutonium ion must result in an appreciable rehybridization of the bonds of the ring-methylene carbon atoms, the observation of a zero isotope effect ($k_H/k_D = 1$) in the ethanolysis and acetolysis of



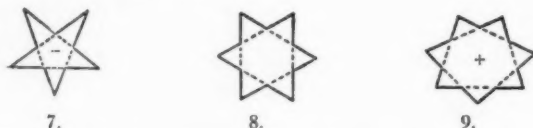
was taken as evidence for the formation of the classical ion in the rate-determining step. It is difficult, however, to account for the reactivity of cyclopropylcarbinyl derivatives without invoking the idea of some participation of the neighbouring cyclopropyl group, and until it can be shown that appreciable bond frequency changes must necessarily accompany the formation of the transition state leading to a non-classical ion, whether it be a cyclobutonium or a homoallylic ion (130), the conclusion based on the isotope effect results must be considered tentative.

Winstein *et al.* (131) have provided strong evidence for the formation of the non-classical tris-homocyclopropenyl cation, structure 5, in the acetolysis of *cis*-3-bicyclo[3.1.0]hexyl tosylate, structure 4. The reaction proceeds

stereospecifically to *cis*-acetate, structure 6, it is 35 times faster than acetolysis of the *trans* isomer, and it shows a special salt effect; these observations are indicative of anchimeric assistance and formation of a cation of special structure. Further, acetolysis of the 3-deuterated bicyclohexyl tosylate results in a scrambling of deuterium, such that the alcohol product derived from the acetolysis has a 2:1 ratio of cyclopropane ring-deuterium to carbinol carbon-deuterium.



The wave-mechanical analogy between the symmetrical cation 5 and the cyclopropenyl cation has prompted the author (132) to suggest the possible formation, as reaction intermediates, of the homoaromatic structures 7, 8, and 9, $[C_{10}H_{18}]^-$, $[C_{12}H_{18}]$, and $[C_{14}H_{21}]^+$, which would be the homo counterparts to the cyclopentadienide ion, benzene, and the tropylium ion, respectively. If such structures could indeed be shown to exist, this would serve as a striking demonstration of the change in ideas that has taken place since simple carbonium ions were first postulated as intermediates in solvolytic processes over 25 years ago.



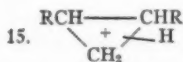
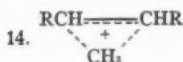
A spectacular case of neighbouring group participation is provided by the very high rate of solvolysis of 7-norbornadienyl chloride (structure 10) (133). A highly delocalized non-classical cation is thus indicated, of which structure 11 is the most extreme suggested. It comprises an eight-electron delocalized system resulting from the interaction of an approximately tetrahedrally hybridized HC^+ group with a benzene ring. The effect on the solvolytic reactivity of norbornene derivatives when a double bond is replaced by a fused benzene ring has been examined by Bartlett & Giddings (134). Whereas the benzene ring assists ionization in the 2-position as effectively as does a double bond, it provides only half the assistance, on an energy scale, for ionization at the 7-position.



Winstein *et al.* (135, 136) have now given a detailed account of the anchimerically assisted solvolyses leading to the "bird cage hydrocarbon" and related compounds. A number of non-classical cations must be postulated to explain the products formed, though certain limitations to the interconversion of these cations are indicated. Similarly, DePuy *et al.* (137) have concluded, from the observed stereospecificity in the solvolysis of *endo*- and *exo*-7-isopropylidenedehydronorbornyl tosylates, that there is a potential energy barrier to the interconversion of the two homoallylic ions 12 and 13. The first direct measurement of the rate constant for the interconversion of two non-classical carbonium ions has been accomplished by Bartlett *et al.* (138) in a kinetic study of the complex transformations of the long-lived, asymmetric, *p*-anisylcamphinilyl cation.

Noyce *et al.* (139) have observed that the acetolysis of *trans*-4-methoxycyclohexyl-1-*t* tosylate leads to *trans*-4-methoxycyclohexyl acetate with a scrambling of tritium between the 1- and 4-positions. This result is interpreted in terms of a bridged oxonium ion intermediate with the cyclohexane ring in the boat conformation (140).

A methyl-bridged carbonium ion, structure 14, has been invoked to account for the formation of cyclopropanes during the nitrous acid deamination of *n*-propylamine (141), and of isoamylamine and 3-methyl-2-aminobutane (142), and during the "de-oxidation" reaction of several alcohols (141). The suggestion was made (141) that a protonated cyclopropane intermediate, structure 15, may intervene between structure 14 and product and that such an intermediate may be involved in other carbonium ion rearrangements. However, C¹³ (143) and deuterium (144) tracer studies have shown that this species is not an intermediate in the rearrangement of the neopentyl carbonium ion under acidic or basic conditions. It is unlikely, therefore, that such species are formed in rearrangements leading to cyclopropanes (145) or in other carbonium ion rearrangements.



The difficulty of adequately representing the electron delocalization in the homoallylic ions formed in the anchimerically assisted solvolysis of penta-methylcyclopentadienylmethyl tosylate (146, 147) points to the need for further clarification of ideas pertaining to the subject of non-classical ions.

ALLYLIC AND RELATED REARRANGEMENTS

Recent developments in allylic rearrangements have been reviewed by Goering (148). Goering *et al.* (149, 150) by an ingenious combination of optical activity and O¹⁸ tracer studies, have shed light on the structure and bonding of the internal ion-pair intermediate that is involved in intramolecular isomeric (S_Ni') rearrangements of allylic compounds. Carbonyl-O¹⁸ labelled *d-trans*- α,γ -dimethylallyl *p*-nitrobenzoate was partially solvolyzed in aqueous acetone and the unsolvolyzed but racemic ester isolated and resolved. The O¹⁸ distribution between carbonyl and ether positions in each

enantiomer was then determined. It was found that the rate of O^{18} scrambling in the enantiomers is 0.35 times as fast as the rate of ester racemization. This suggests that an energy barrier separates the two equivalent structures (Fig. 1)

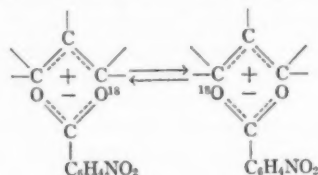


FIG. 1.

and that this barrier is only slightly greater than that for internal return to *dl*-ester. On the other hand, *trans*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate-carbonyl- O^{18} undergoes equilibration of the label between ether and carbonyl positions faster than it racemizes, indicating that ionization gives rise in part to an ion-pair intermediate in which both oxygen atoms are closer to C_a than to C_γ . The reason for this difference in behaviour of the two compounds is not immediately apparent.

Sneen (151) has shown from kinetic data that the difference in the free energies of activation for the total reaction (solvolysis and intramolecular rearrangement) of α -aryl- γ -methylallyl *p*-nitrobenzoate and α -methyl- γ -arylallyl *p*-nitrobenzoate is almost entirely attributable to the difference in ground state energies. This result is consistent with a mechanism in which the product of the initial rate-determining step for each isomer is a high-energy intermediate (ion-pair) which both transition states would be expected to resemble closely in geometry and in energy content (152).

Bordwell *et al.* (153) have now published a kinetic study of the S_N2' reaction of 3-halomethylbenzothiophene 1,1-dioxide with thiourea. The factors favouring S_N2' reaction in this system are activation by the $ArSO_2$ group and the fact that the only conformation possible for displacement is the one favourable to S_N2' reaction. Strong support for the concerted nature of this reaction is given by the observation that the relative reactivities of RCl , RBr , and RI for this S_N2' reaction (1:80:230) are similar to those observed for S_N2 displacements of allylic halides.

Marvell & Stephenson (154) have shown that the stereochemical course of the Claisen rearrangement can be satisfactorily explained by assuming a cyclohexane type transition state and applying to it the principles of conformational analysis. This interpretation is in accord with results of similar stereochemical work by Burgstahler (155) and with the finding of Norcross & White (156) that bulky substituents in the β -position do not retard the rate of rearrangement.

ELIMINATION REACTIONS

Nature of the transition state in E2 reactions.—Recent studies have served to demonstrate that charge distribution and the relative extent of C—H and

C—X bond stretching in the transition state of the bimolecular elimination (E2) reaction may vary greatly with changes in the leaving group, the solvent, and the base. Saunders & Edison (157) have measured the β -deuterium isotope effect and DePuy & Bishop (158) have determined the Hammett ρ values for the E2 reaction of 2-phenylethyl derivatives with ethoxide and *t*-butoxide ions. The variation of these quantities with leaving group for reaction with ethoxide ion at 30°C. is shown in the following tabulation:

Leaving Group	k_H/k_D	ρ
Br	7.11	2.14
OTs	5.66	2.27
S(CH ₃) ₂	5.07	2.75

The deuterium isotope effects, which are considered to be a measure of C—H bond stretching in the transition state, are in the order Br > OTs > S(CH₃)₂; whereas the ρ values, which are a measure of the development of negative charge on the β -carbon and its attached aryl group, are in the reverse order. This seemingly anomalous result can be rationalized on the basis that the extent of C—X bond stretching in the transition state, and hence the degree to which negative charge is accommodated on the leaving group, is greatest for the bromide and least for the sulfonium salt. That the sulfonium salt elimination indeed has a high carbanionic character is evident from the small sulfur isotope effect observed by Saunders & Ašperger (159) for the reaction. On the other hand, Ayrey & Bourns have found a nitrogen isotope effect of 1.3 per cent at 30°C. in the Hofmann elimination of the corresponding ammonium salt [cited in (14)]. Since this effect is about one third the theoretical maximum, an appreciable C—N bond stretching in the transition state is indicated.

Orientation in E2 reactions.—Conflicting theories have been proposed in the past to account for orientation in E2 reactions. Hughes & Ingold have interpreted the direction of elimination, as well as reaction rates, mainly in terms of a competition between hyperconjugative and inductive influences, whereas Brown has considered the opposing factors to be hyperconjugative and steric. Banthorpe, Hughes & Ingold (160, 161) have now reported the results of a detailed study of the kinetics of the reactions of several series of alkyl dimethylsulfonium and alkyl trimethylammonium salts with ethoxide in ethanol, and with *t*-butoxide in *t*-butyl alcohol. The observed relationships between alkyl group structure and the free energies of activation would appear to be satisfactorily accounted for in terms of inductive effects alone until the alkyl group reaches the complexity of 3,3-dimethylbutyl, when the influence of a steric effect finally becomes apparent. Calculation of compression energies has served to indicate that, of the various types of steric interactions possible in this particular structure, only the one involving interactions between the β -*t*-butyl group and the leaving group would be expected to be of sufficient magnitude to account for the steric contributions to the activation energies.

Becker (162) has attempted to evaluate the role of steric effects in E2 reactions by calculating the "steric partition functions" for the isomeric transition states leading to the 1- and 2-olefins. His results are in conflict with the conclusions of Banthorpe *et al.* (160) in several important respects; in particular, they indicate that the steric requirements of the attacking base can be expected to play an important role in determining the direction of elimination. On the other hand, both methods of calculation clearly demonstrate that the steric requirements of the leaving group are relatively unimportant and that, presumably, the inductive effect is mainly responsible for the marked increase in the proportion of 1-olefin in going from halides to onium salts. This interpretation is consistent with conclusions relating to the nature of the transition states for the two classes of compounds (*vide supra*). In halide eliminations the double bond is well developed and hyperconjugation favouring 2-olefin is important; in onium salt reactions the transition state has high carbanionic character and, consequently, hyperconjugative effects are minimized and the retarding influence of inductive effects is controlling.

Also consistent with the conclusions relating to the role of the leaving group in determining orientation is the finding of Saunders *et al.* (163) that in the E2 reaction of 2-pentyl and 2-methyl-2-butyl halides the proportion of 2-olefin varies in the order $\text{Cl} < \text{Br} < \text{I}$. This is in the opposite direction to that predicted on the basis of the steric requirements of the leaving group, but it can be readily understood in terms of an increasing tendency for formation of the more stable olefin as the double-bond character of the transition state increases with increasing ease of heterolysis of the $\text{C}-\text{X}$ bond.

An anomalous case of orientation in the E2 reaction of onium salts is found in the formation of 3-menthene as the main product of the Hofmann degradation of neomenthyltrimethylammonium ion. This has been attributed by Hughes & Wilby (164) to reaction via a transition state in which $\text{C}-\text{N}$ bond rupture is well advanced, that is, a transition state of high carbanium ion character.

Carbanion vs. concerted mechanisms.—It has been assumed that the *cis*-elimination of haloalkenes to acetylenes involves the formation of a *trans*-vinyl carbanion that isomerizes to its *cis*-isomer before loss of halide ion. Miller & Lee (165) have now found that *cis*- and *trans*-1,2-dihaloethenes undergo hydrogen exchange more rapidly than elimination, and they have established a lower limit of 25 to 35 kcal./mole to the activation energy for isomerization of the vinyl carbanions derived from these compounds. Convincing arguments are advanced for a *cis*-elimination mechanism in which the *trans*-carbanion undergoes direct loss of halide ion (Fig. 2).

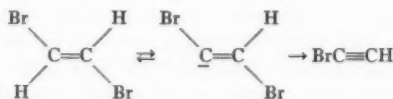


FIG. 2.

Most compounds that undergo base-catalyzed elimination show a very small or negligible hydrogen exchange under the elimination reaction conditions and therefore may be reacting either by a concerted mechanism or by a two-step process with removal of the proton forming a carbanion intermediate rate-determining. Buncl & Bourns (14) have successfully distinguished between the two mechanisms for the carbonyl elimination reaction (E_{CO2}) of benzyl nitrate forming benzaldehyde on the basis of the following observations: (a) no deuterium exchange, (b) a normal nitrogen isotope effect ($k_{14}/k_{15} = 1.020$), and (c) a normal deuterium isotope effect ($k_H/k_D = 5.0$). Only the concerted mechanism is in accordance with these results. A comparison of the isotope effects and ρ values for the reaction with corresponding quantities for olefin-forming elimination processes suggests that, with respect to the extent to which bonds are weakened, the transition state for the E_{CO2} reaction is intermediate between the transition states for an $E2$ reaction of β -phenylethyltrimethylammonium ion and β -phenylethyl bromide.

Cristol & Stermitz (166) have made a kinetic study of the $E2$ reactions of *cis*- and *trans*-2-phenylcyclohexylammonium and sulfonium ions with ethanolic potassium hydroxide. Comparison of rates with those of the acyclic (2-phenylethyl) analogs shows that the *trans*-elimination of the *cis*-ammonium compound is abnormally slow, and the *cis*-elimination of the *trans*-sulfonium compound is abnormally fast. The former is considered to be a consequence of the energy required to force the bulky $N(CH_3)_3^+$ group into the axial position required for the formation of the *trans* coplanar transition state, while the latter is attributed to a facile multistage process involving formation of a zwitter ion (ylide) intermediate by removal of a proton from an α -carbon atom.

Pyrolytic elimination reactions.—A comprehensive review of this subject has been provided by DePuy & King (167).

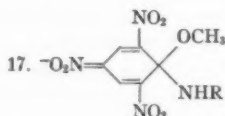
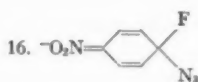
Kingsbury & Cram (168) have made a careful kinetic and stereochemical study of the pyrolytic elimination reactions of the four diastereoisomers of 1,2-diphenyl-1-propyl phenyl sulfoxide. The results indicate that more than one primary process is involved. It is suggested that at low temperatures the reaction proceeds by the cyclic concerted mechanism characteristic of *cis*-elimination processes (167), while at higher temperatures a second primary process, giving a radical pair, becomes increasingly important. This interpretation may have important implications with regard to the mechanism of other pyrolytic elimination processes.

NUCLEOPHILIC SUBSTITUTION AT UNSATURATED CARBON

Nucleophilic aromatic substitution by the addition mechanism.—This topic has recently been reviewed by Sauer & Huisgen (169).

Although the two-step mechanism in activated substitution has been amply demonstrated by kinetic techniques, the direct evidence on the existence of intermediates recently reported forms a valuable confirmation of the mechanism. Miller *et al.* (170), in a study of the reaction of *p*-fluoronitrobenzene with sodium azide in dry dimethylformamide, have shown that al-

though azide ion is consumed in a first-order process, no fluoride ion is formed, and a characteristic spectral absorption makes its appearance at the same rate. Addition of water results in the formation of *p*-azidonitrobenzene and fluoride ion, with the disappearance of this spectral absorption. These results constitute strong evidence for the formation of an intermediate complex, structure 16, stabilized in the absence of a suitable solvating medium for the anion.



Farmer (171), working with more activated systems, has actually been able to isolate a series of stable quinonoid nitronates, structure 17, which may be prepared either by the action of methoxide ion on trinitrophenylamines, or by the action of amines on methoxytrinitrobenzene.

Lewis & Suhr (172) have shown that substitution of halogen by thiocyanate in *para*-halogen substituted benzenediazonium ions follows the rate order $I > Br > Cl > F$. This is the reverse of the order that normally prevails in nucleophilic aromatic substitution and is attributed to the high polarizability of the thiocyanate ion and the poor solvating power of the solvent *t*-butyl alcohol. An alternative explanation of the results is, however, that breakdown of the intermediate is rate-determining.

Substitution in the *p*-phenylene-bis-diazonium ion proceeds at abnormally high rates and the transition state is believed to involve bonding of the attacking nucleophile both to carbon and to the terminal nitrogen of the group to be displaced (173).

Benzyne intermediates.—Recent developments in the study of the elimination-addition mechanism for nucleophilic aromatic substitution have been reviewed by Huisgen (174, 175). Quantitative studies by this author and his co-workers (176) on the selectivity of the benzyne intermediate in its reactions with different reagents have placed this mechanism for the reaction of non-activated aryl halides on an even firmer basis. Competition experiments carried out in ether with a tenfold excess of phenyllithium and lithium piperidide in varying proportions show that benzyne adds phenyllithium 4.4 times faster than it adds lithium piperidide. The fact that this rate ratio is the same regardless of whether fluorobenzene or chlorobenzene is the reactant demonstrates that the selective intermediate does not contain halogen. On the other hand, in the formation of benzyne, as measured by the rate of liberation of halide ion in ether at 20°C., lithium piperidide is more efficient than phenyllithium, by factors of 27 in the case of fluorobenzene and 70 in the case of chlorobenzene. Similar competition studies with 1,2-naphthalene and 9,10-phenanthryne yielded rate constant ratios of 5.8 and 12.8, respectively, in favour of phenyllithium. This increasing selectivity towards bases in the series benzyne, 1,2-naphthalene, and 9,10-phenanthryne, reflects a

corresponding increase in stability of the intermediates and appears to be directly related to the decreasing C—C bond lengths involved.

Competition experiments between the bases (lithium-N-methylanilide, A; piperidine, B; and lithium piperidide, C) with 9,10-phenanthryne show that A reacts 0.36 times as fast as B which in turn reacts at the same rate as C (177). It is highly noteworthy that B and C, which differ in basic strength by *ca.* 25 *pK* units, should be equally reactive toward 9,10-phenanthryne.

Panar & Roberts (178), by a combination of deuterium isotope effect and C^{14} tracer studies, have provided convincing evidence against the operation of mechanisms other than benzyne formation in the amination of non-activated halobenzenes. These authors have also demonstrated, by their observation of a kinetic isotope effect in the reaction of 3-bromoanisole-2,4,6- d_3 , that the non-rearranging amination of 3-substituted halobenzenes also proceeds through a benzyne intermediate.

Perchloryl aromatic compounds, $ArClO_3$, have been shown to give rise to benzyne on treatment with sodamide or phenyllithium (179). The predominant elimination of chlorate ion in preference to halogen during the reactions of *p*-halogenoperchloryl compounds has been attributed both to the high electronegativity of the chlorate group (with consequent acidity of the *o*-hydrogens) and to its good anionic leaving ability.

Stiles *et al.* (180, 180a) have obtained evidence for the formation of benzyne as an intermediate in the decomposition of benzenediazonium-2-carboxylate. The inner salt loses nitrogen and carbon dioxide and forms a Diels-Alder adduct when heated with furan or with anthracene in benzene solution, while flash photolysis of the compound gives rise to a transient spectral absorption ($\lambda_{max} \approx 241\text{ m}\mu$) and forms biphenylene as the major product. The latter observations have been tentatively ascribed to the formation of gaseous benzyne.

Montgomery & Roberts (181) have found that, in the formation of 1-phenylcyclopentene by reaction of phenyllithium with 1-chlorocyclopentene-1- C^{14} , half of the label remains on C_1 and the remainder is distributed on adjacent carbon atoms. This result is compatible with the formation of the cyclopentyne intermediate. Wittig *et al.* (182) have been able to trap cyclopentyne as a Diels-Alder adduct.

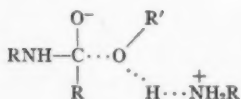
Substitution at vinyl carbon.—Recent work in this field has been concerned with the problem of distinguishing between the intermediate-complex and concerted mechanisms. Modena *et al.* (183, 184, 185), in a study of the substitution of halogen in arylsulfonylhalogenoethylenes, $ArSO_2CH=CHX$, by nucleophilic reagents in methanol, have observed the absence of an "element effect" in the *trans*-series, viz., $k_{Br}/k_{Cl} \approx 1$ to 2. In the *cis*-series, k_{Br}/k_{Cl} has again the same low value with reagents $C_6H_5S^-$ and N_3^- , but is greater than 100 with RO^- ; in the latter case, however, some elimination product, $ArSO_2C \equiv CH$, is formed. The authors conclude that two mechanisms are followed in these substitutions: (a) when $k_{Br} \approx k_{Cl}$, a two-

step mechanism with a rate-determining formation of an intermediate, $[\text{ArSO}_2\dot{\text{C}}\text{H}-\text{CHXY}]^-$, followed by a fast expulsion of halogen; and (b) when $k_{\text{Br}} \gg k_{\text{Cl}}$, an elimination-addition mechanism that can occur only with strongly basic reagents in systems (*cis*-derivatives) in which *trans*-elimination is possible. The intermediate complex mechanism for activated substitution is confirmed by the stereochemical studies of Vernon *et al.* (186) on the displacement of halogen in *cis*- and *trans*-ethyl- β -chlorocrotonates.

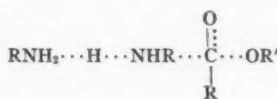
Substitution in less activated systems has been studied by Carrà & Beltrame (187). Although the $k_{\text{Br}}/k_{\text{Cl}}$ ratio for displacement of halogen from $(\text{C}_6\text{H}_5)_2\text{C}=\text{CHX}$ has the value four, the activation energies (38 and 30 kcal.) are much higher than those in the studies of Modena and Vernon (15 to 20 kcal.). Thus, if an intermediate is formed in these systems it must be a very high energy one.

Substitution at acyl carbon.—The mechanisms of catalysis of nucleophilic reactions of carboxylic acid derivatives have been reviewed by Bender (188). The factors affecting the reactivity of nucleophilic reagents toward esters have been examined by Jencks & Carriuolo (189).

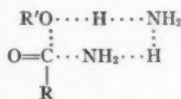
The reaction of esters with amines has been studied by three groups of workers (190, 191, 192) and each group observed generalized base catalysis, a result that cannot be accommodated by the Hammett mechanism (193). Three kinetically equivalent mechanisms are now given. Bunnett & Davis (190) propose, for the reaction of ethyl formate with *n*-butylamine in ethanol, the formation of tetrahedral intermediates in pre-equilibrium steps, followed by a slow, general acid-catalyzed removal of the alkoxy group (transition state 18 for amine catalysis). The mechanism favoured by Jencks & Carriuolo (191) for the aminolysis and ammonolysis of phenyl acetate in aqueous solution involves the removal, in a concerted process, of a proton from the molecule of attacking amine by a second molecule of amine (transition state 19). Bruice & Mayahi (192), in a study of the ammonolysis of substituted phenyl acetates in aqueous solution, propose a mechanism in which attack by NH_3 on carbonyl carbon is assisted by proton abstraction while departure of OR' is assisted by proton transfer from a second NH_3 molecule (transition state 20).



18.



19.



20.

It is clearly difficult, on the basis of existing evidence, to decide between the three possibilities. Although tetrahedral intermediates are now generally considered to be involved in the displacement reactions of carboxylic acid derivatives (188), the possibility of a completely concerted process cannot be excluded in particular reaction systems.

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MARINE GEOCHEMISTRY¹

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An appreciation of the complex and oftentimes enigmatic chemistries occurring within the world's oceans, the largest aqueous chemical system on earth, may be found in considerations of the rather curious compositions and the natures and distributions of reaction sites within the marine environment. The oceans contain chemical species of all of the elements, yet only 12 have concentrations equal to or greater than a part per million by weight. In general these major elements are relatively non-reactive. The more reactive elements, whose chemistries are in the sub-micromolar range, are involved in reactions that give rise to discernible amounts of products over long time periods—from days to thousands of years.

Most of the reactions occur at phase discontinuities, the water-atmosphere, water-biosphere or water-sediment interfaces. Because most oceanic waters attained nearly all of their dissolved species thousands of years ago, equilibration of such substances might be expected. However, the fact that large masses of ocean waters are out of contact with reaction surfaces provides an explanation for such thermodynamically unstable species as manganous, iodide, and arsenite ions, which enter the oceans as such reduced species or arise from biochemical reactions.

This survey of recent developments in marine geochemistry will emphasize the chemical reactions occurring within the oceans and the parameters that influence the course of such reactions. Since the last general collation of the chemical and physical properties of seawater in 1946 (1), a large volume of literature has appeared; this has been digested into several rather restricted books and reviews. *The Chemistry and Fertility of Sea Waters* by Harvey (2) is an extensive treatment of the biochemical processes and their influence upon the chemical composition of marine environments. Two summaries considering the physical and chemical properties of ocean waters have appeared (3, 4); both are directed towards quite general oceanographic problems. Finally, Barnes (5) has compiled the methods and techniques of analyses of sea water; however, his book is limited to classical methodology and does not consider the more modern analytical tools.

PHYSICO-CHEMICAL PARAMETERS OF THE MARINE ENVIRONMENT

Equation of state.—Eckart (6) has shown that in a temperature range of 0° to 40°, a pressure range of 0 to 1000 atm., and a salinity range of 0 to 40 g./kg. the empirical isotherms of sea water can be adequately represented by

$$(\rho + \rho_s)(\Delta_s - \Delta) = K$$

¹ The survey of literature pertaining to this review was concluded November 1, 1960.

where p is the pressure in atmospheres, and $\Delta = 10^4 (1 - v)$, where v is the specific volume expressed in ml./g. Of the three constants, only Δ_0 is independent of salinity and temperature and has the value of 3020. The other two constants are given as:

$$p_0 = 5890 + 38T - 0.375T^2 + 3S$$

$$10^{-6}K = 17.795 + 0.1125T - 0.000745T^2 - (0.0380 + 0.00017T)S.$$

Specific heat.—Between -2° and 30°C . the specific heat of pure water decreases with increasing temperature whereas this effect is reversed with sea waters having more than 20 parts per thousand of salt (7). An expression for the specific heat at any temperature and salinity, based upon experimental data, was derived as follows:

$$C_p = A - 0.005075S - 0.000014S^2$$

where C_p is the specific heat in joules/g., S the salinity in g./kg., and A is the specific heat at constant pressure of pure water at the temperature $T + 0.7S + 0.0175S^2$ in $^\circ\text{C}$.

Colligative properties.—Isopiestic determinations of the vapor pressures of sea waters of varying salinities at 25°C . were made by Robinson (8) who found the following equation:

$$(p^0 - p)/p^0 = 0.0009206(\text{Cl}) - 0.00000236(\text{Cl})^2$$

where p^0 is the vapor pressure of pure water and Cl the chlorinity expressed in parts per thousand. The equation held for a range of chlorinities between 9 and 22 per thousand. Arons & Kientzler (9) determined the vapor pressures of sea water solutions at temperatures between freezing and 25°C . for chlorinities between 5 and 160 per thousand. From their data it is found that the boiling point is elevated 0.018°C . for each unit of chlorinity in parts per thousand. Assur (10) gives, on the basis of data from Nelson & Thompson (11), for the depression of freezing point of sea water of salt content, Z (g. of salt per kg. of water) as $t = -Z/0.1848$ for values of Z between 0 and 150.

Thermodynamic functions.—A systematic thermodynamic study of the sea water system has been curiously absent from oceanographic literature. This situation stems not only from the complex nature of such a multi-component system but also from the difficulties in the treatment of non-equilibrium processes that occur in nature. Fofonoff (12) has provided the initial entry into a thermodynamic treatment of sea water with emphasis upon applications to the dynamics of the ocean system. Craig (13) has challenged the validity of several aspects of this study, modifying erroneous treatments of the gravitational field function and the chemical potential. It seems advantageous today to consider sea water as a two-component system of NaCl and H_2O for most applications of thermodynamics to oceanographic problems. A simple basis for relating salinity to molality of NaCl solutions may be found by assuming the equivalence of NaCl and sea water solutions that possess the same vapor pressure. Robinson (8) tabulates all necessary data for such conversion.

COMPOSITION OF THE MARINE ENVIRONMENT

During the last decade a great deal of effort has been devoted to delimiting the composition of the marine environment. A number of elements in trace concentrations, which had previously escaped quantitative determination, were assayed. Much of this work stemmed from the application of new analytical techniques such as isotope dilution and activation analysis. Isotopic analyses of some of the lighter elements introduced new parameters for marine geochemical investigations, while studies on both artificially produced and naturally occurring radioisotopes were extensive. But perhaps of greater significance to studies of chemical reactions in the oceans has been the decided emphasis upon a knowledge of the chemical speciation of elements in sea water—studies that have been derived from recent advances in inorganic chemistry.

Elemental composition.—Table I gives the most recent picture of the elemental composition of sea water as compiled from the original literature, and includes the major chemical species present, adapted primarily from Sillen (14) and complimented with the data of other workers (15 to 18). Elements whose marine concentrations have been determined for the first time recently include: Be (15); Ti (19, 20); Cr (20, 21); Ga (22); Ge (22); Nb (23); Cd (24); W (25, 26); and Pa (27).

The listed concentrations (Table I) are for an average sea water with a chlorinity of 19 parts per thousand by weight; however, some may not be truly representative because they result from a single set of observations, normally in surface waters, or are averages of several investigators whose results are not in complete agreement. It has long been known that chemical species of those elements (C, N, O, P, S, and Si) involved in primary plant production and in the subsequent combustion of organic matter show marked concentration changes as a function of time, depth in the water column, or location in the world's oceans. Differences in abundances by nearly three orders of magnitude have been reported (28).

Recent investigations also indicate ocean to ocean and depth variations for elements not directly involved in photosynthesis and for the so-called conservative elements, whose concentrations are presumed directly proportional to the chlorinity. Gast & Thompson (29) report small changes in the concentration of boron, considered a conservative element, relative to the chlorinity. They attribute such differences to varying concentrations of polyhydroxy organic compounds, which strongly complex with the chemical species of boron in sea water. Later, Gast (30) found slight permutations upon the surface values of the ratio that apparently result from the extent of evaporation undergone by the water mass or the amounts of precipitation or river run-off introduced. The boron/chlorinity ratio in rain water is often hundreds of times larger than the sea water value. Such observations are related to the evaporation of boric acid from sea water (26).

Measurements by Koczy (31) in the Pacific, Indian, and Atlantic Oceans indicate a consistent increase of radium-226 with depth. He postulated that the radium originates from the radioactive decay of its parent ionium (thor-

TABLE I
CHEMICAL COMPOSITION OF SEA WATER WITH MAJOR SPECIES FOR EACH ELEMENT

Element	Concentration in mg./l.	Species present	Element	Concentration in mg./l.	Species present
H	108,000	H ₂ O	Se	0.004	SeO ₄ ²⁻
He	0.000005	He(g.)	Br	65	Br ⁻
Li	0.2	Li ⁺	Kr	0.0003	Kr(g.)
Be	0.0000006	Be(OH) ⁺ ; Be(OH) ₂	Rb	0.12	Rb ⁺
B	4.6	B(OH) ₃ ; B(OH) ₂ O ⁻	Sr	8	Sr ⁺⁺ ; SrSO ₄
C	28	HCO ₃ ⁻ ; H ₂ CO ₃ ; CO ₃ ²⁻ ; org. cpds.	Y	0.0003	
N	0.5	NO ₃ ⁻ ; NO ₂ ⁻ ; NH ₄ ⁺ ; N ₂ (g.); org. cpds.	Nb	0.00001	
O	857,000	H ₂ O; O ₂ (g.); SO ₄ ²⁻ and other anions.	Mo	0.01	MoO ₄ ²⁻
F	1.3	F ⁻	Tc-Pd		
Ne	0.0001	Ne(g.)	Ag	0.0003	AgCl ₂ ⁻ ; AgCl ₂ ²⁻
Na	10,500	Na ⁺	Cd	0.00011	Cd ⁺⁺ ; CdSO ₄
Mg	1,350	Mg ⁺⁺ ; MgSO ₄	In	<0.02	
Al	0.01		Sn	0.003	
Si	3	Si(OH) ₄ ; Si(OH) ₃ O ⁻	Sb	0.0005	
P	0.07	HPO ₄ ²⁻ ; H ₂ PO ₄ ⁻ ; PO ₄ ³⁻ ; H ₃ PO ₄	Te		
S	885	SO ₄ ²⁻	I	0.06	IO ₃ ⁻ ; I ⁻
Cl	19,000	Cl ⁻	Xe	0.0001	Xe(g.)
A	0.6	A(g.)	Cs	0.0005	Cs ⁺
K	380	K ⁺	Ba	0.03	Ba ⁺⁺ ; BaSO ₄
Ca	400	Ca ⁺⁺ ; CaSO ₄	La	0.0003	
Sc	0.00004		Ce	0.0004	
Ti	0.001		Pr-Ta		
V	0.002	VO ₂ (OH) ₂ ⁻	W	0.0001	WO ₄ ²⁻
Cr	0.00005		Re-Pt		
Mn	0.002	Mn ⁺⁺ ; MnSO ₄	Au	0.000004	AuCl ₄ ⁻
Fe	0.01	Fe(OH) ₃ (s.)	Hg	0.00003	HgCl ₂ ⁻ ; HgCl ₄ ²⁻
Co	0.0005	Co ⁺⁺ ; CoSO ₄	Tl	<0.00001	Tl ⁺
Ni	0.002	Ni ⁺⁺ ; NiSO ₄	Pb	0.0001	Pb ⁺⁺ ; PbSO ₄
Cu	0.003	Cu ⁺⁺ ; CuSO ₄	Bi	0.0002	
Zn	0.01	Zn ⁺⁺ ; ZnSO ₄	Po, At		
Ga	0.00003		Rn	0.6 × 10 ⁻¹⁸	Rn(g.)
Ge	0.00007	Ge(OH) ₄ ; Ge(OH) ₃ O ⁻	Fr		
As	0.003	HAsO ₄ ²⁻ ; H ₂ AsO ₄ ⁻ ; H ₃ AsO ₄ ; H ₄ AsO ₄	Ra	1.0 × 10 ⁻¹⁸	
			Ac		
			Th	0.0007	
			Pa		
			U	0.003	UO ₂ (CO ₃) ₂ ²⁻

ium-230) in the sediments, with a subsequent diffusion upwards through the water column. Ionium is rapidly removed from sea water after its formation in the uranium-238 decay series and accumulates in the deep-sea deposits where it is thought to be quite strongly bonded to the solid phases. Radium, on the other hand, is presumed to be in an ionic form and able to diffuse readily through the sediment pore-waters.

Similarly, the barium concentrations in the oceanic water column increase with depth (32). Several mechanisms have been proposed that would result in a net transfer of the barium from the surface to deeper levels in the oceans. During the oxidation of detrital organic phases, high levels of sulfate ions are produced within the decomposing micro-environment where a precipitation

of barium sulfate could occur. The barium sulfate crystals sink through the water column and dissolve at lower depths where the sulfate ion concentration is within its normal range. A second transfer process involves the direct release of barium ion in the decaying organic phases which are known to enrich barium over sea water by factors of 450–4400 (33). Finally, it is conceivable that barium, incorporated in the sedimentary components, diffuses into the oceans. On the other hand, the increasing radium concentrations (with depth) in the upper levels of the ocean may be partly attributable to such biochemical processes as have been proposed for barium.

Copper is one of the most extensively analyzed trace elements in the oceans, and values for its concentrations in the surface waters of the Atlantic and Pacific appear to differ by an order of magnitude. The copper contents in the Atlantic appear to cluster about 10 or 20 $\mu\text{g./l.}$: 6.4, Scottish coast (34); 12, English Channel (35); 22, English Channel (36); 1, Scottish coast (37); 27, Irish Sea (38); 19, English Channel (38); 6, Adriatic Sea (39); 16, Massachusetts coast (40); and 17, Atlantic coast (41). The majority of concentrations of copper for Pacific waters are of the order of several micrograms/liter: 1–2, Washington coast (42, 43); 1–6, Tokyo Bay (44); 3, Japanese coast (45); 1, Japanese coast (46); 0.6, open ocean off Japan (46); and 2.4, Tokyo Bay and environs (47). Since none of the above investigations obtained adequate, if any, samples from deep waters, it is difficult to relate these regional differences to either biological or inorganic processes. It seems that further work on the distribution of copper will prove most rewarding.

Several observations in chemical speciation problems in sea water have been the focal points of controversy. Baas-Becking *et al.* (48) put forth the rather startling result that the thermodynamically unstable perchlorate ion existed in ocean waters off Australia in concentrations between 150 and 300 mg./l. Their work suggested that perchlorate concentrations tended to be highest near the coast and to decrease far from land and at great depths. This alleged occurrence was not confirmed by Greenhalgh & Riley (49) who examined both surface and deep water samples from the Arctic Ocean, North Atlantic, English Channel, Mediterranean, Indian Ocean, Red Sea, and Persian Gulf and stated an upper limit of 0.03 mg./l. for the perchlorate ion concentration.

Shaw & Cooper (50, 51) have suggested that the oxidized form of iodine in sea water is hypiodous acid rather than the thermodynamically stable iodate ion. They argue that the high iodine content in air above sea water is explainable by the reaction of hypiodous acid and iodide ion, normally present in sea water, to produce trace amounts of volatile iodine in the elemental form. Further, they point out that the presence of reducing organic matter will prevent any iodate accumulation and that the rate of iodate formation from hypiodous acid, a third-order reaction in near-neutral solution (pH of sea water varies about 8), will be quite slow at the low hypiodous concentrations of sea water (presumed to be of the order of 10^{-7} molar).

This hypothesis has been challenged by several investigators (52, 53) who

were unable to experimentally detect hypiodous acid in sea water. Further, they observed that the system iodide, iodine, hypiodite, and iodate quite rapidly reaches thermodynamic equilibrium with the two states iodide and iodate.

The ubiquitous presence of thermodynamically unstable iodide in sea water (18) invites investigations seeking out the factors that govern the oxidation states of iodine. It is difficult to escape the conclusion that the marine biosphere must be intimately involved in the cycle of this element. Plants and animals contain the reduced iodide in iodo-tyrosines and thyroxine. Which forms of iodine do they assimilate from the marine environment? Which forms are generated back to the sea upon the destruction of the organic phases?

Dissolved organic matter.—The nature of the dissolved organic substances in sea water, contributed by the many biochemical cycles, remained unresolved until recently. Although the total amounts of organic carbon in the open ocean had been clearly shown to lie between 0.2 and 3.0 mg./l. (54 to 61), for the most part the characterization of such materials was limited to general classes of compounds or to restricted and oftentimes unique environments. Compounds identified as carbohydrates on the basis of colorimetric reactions with N-ethyl carbazole or anthrone have been reported with concentrations up to 100 mg./l. for near shore surface waters but with much smaller values for off shore deep waters (62 to 66). Organic compounds with P (67, 68, 69), Fe (70), and B (29) have been postulated on the basis that in the analyses of these elements higher amounts are found in strongly oxidized sea waters than in untreated samples. The oxidation is presumed to destroy the organic species containing the element in question. Creac'h (71) has claimed evidence for the occurrences of citric and malic acids in the littoral waters off Southern France to levels of several tenths of a mg./l., while Koyama & Thompson (72) have found, in surface waters off the Washington coast, acetic, formic, lactic, and glycolic acids that the authors believe may in large part represent breakdown products of larger molecular weight compounds during the extraction process.

Organic compounds of two general classes, the fatty acids and the vitamins, have been identified, and quantitative determinations of their abundances have been ascertained. Slowey *et al.* (73) found the C-10, C-12, C-14, and C-18 saturated, and the C-14 and C-16 mono-unsaturated fatty acids in Gulf of Mexico waters to depths of 900 m. The total amounts of such acids, weighed as their methyl esters, were about 0.5 mg./l. Williams (74) identified by gas phase chromatography and infrared spectroscopy the saturated C-10, C-12, C-14, C-16, C-18, C-20, and C-22, the mono-unsaturated C-16 and C-18 and the di-unsaturated C-18 acids from Pacific ocean waters to depths of 3000 m. The total acid concentrations varied between 0.014 and 0.12 mg./l. with maximum values at levels between 91 and 1381 m. The saturated C-16 acid was the dominant member of this group and the concentrations of the other saturated acids fell off with both increasing and decreasing numbers of

carbon atoms. Williams also found some structurally unidentified, hydroxylated carboxylic acids having an average molecular weight of 395. They showed no aromaticity and from their C^{13}/C^{12} ratios it was apparent that they were derived from the marine biosphere.

Among the vitamins, B-12 has been most extensively analyzed (75 to 80), and values up to 20 nanog./l., that is, milli- μ g./l. have appeared although concentrations one order of magnitude less are more common. Other vitamins found in sea waters include 0 to 20 nanog./l. of thiamin (80) and 2 to 4 nanog./l. of biotin (81).

It is quite significant that the only detailed study of the vertical distribution of B-12 (79) indicates that the higher values, with a mean of 2.26 nanog./l., were found at intermediate depths of 190 to 2110 m. Above and below this depth interval the mean concentration was 0.57 nanog./l. Such behavior is similar to that observed for the fatty acids and the total dissolved organic matter (57). While the total organic matter is two- or threefold greater in the intermediate depths where the dissolved oxygen gas exists at its lowest levels, the fatty acids and Vitamin B-12 are nearly 10 to 20 times higher. Clearly, the various components of the dissolved organic matter show varying degrees of resistance to oxidation. Since the fatty acids represent less than 10 per cent of the total dissolved organic species, and the vitamins a negligible amount, the most resistant components are yet to be recognized.

Radioactivity.—Two naturally produced radioisotopes were initially found in the marine environment and as yet have not been detected in terrestrial domains. Both isotopes, Be^{10} and Si^{32} , are produced by the cosmic-ray fragmentation of upper atmospheric gases, Be^{10} from nitrogen and Si^{32} from argon. The beryllium isotope with a half life of 2.5×10^6 years was found in the deep-sea sediments of the Pacific Ocean (82, 83), while Si^{32} with a half life of 710 years was observed in the siliceous skeletal material of sponges that lived in the surface waters of the ocean (84). In both cases the oceans provided unique sites for the accumulation of these radioactive species in amounts that are readily assayable by low-level counting techniques. The isotopes arrive at the earth's surface in atmospheric precipitation but are heavily diluted in the relatively large amounts of stable silicon and beryllium on continental surfaces; whereas, in the oceans, the quantities of stable beryllium and silicon, at least in surface waters, are very much smaller and allow the specific activities to attain reasonably high values. Both isotopes show promise for geochronological studies of marine sediments: Be^{10} for the slowly accumulating deep-sea clays and Si^{32} for the more rapidly depositing siliceous oozes. Preliminary results with Be^{10} have been disappointing (15) as the expected uniform decrease in its activity with depth in the sediments was not found.

Two more familiar cosmic-ray produced radioisotopes, C^{14} and H^3 , have been utilized primarily to study oceanic mixing processes. Both isotopes are introduced into the ocean by precipitation, subsequent to atmospheric production, and their specific activities in different oceanic water masses are presumed to reflect solely physical mixing. Broecker *et al.* (85) have sum-

marized the existing measurements for C^{14} , corrected for the C^{14} added by bomb tests and for CO_2 introduced into the atmosphere by the burning of fossil fuels. Many steady state oceanic circulation models have been proposed (85 to 89) but that of Broecker *et al.* (85) has incorporated all existing data into a more detailed picture. Their results suggest, for example, that most of the water below 600 m. in the North Atlantic remains at the depth an average of 650 years, whereas the water masses of Antarctic origin are less than 350 years old. Data for the Pacific are too few and scattered as yet for such calculations.

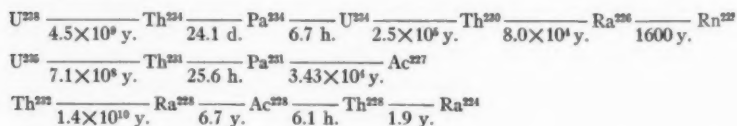
Tritium measurements on ocean water samples (90, 91, 92) have been complicated by the introduction of large quantities of the isotope with the onset of fusion bomb detonations. Although there was not a widespread coverage of analyses prior to the tests, the values did indicate very short mixing times (of the order of five years) for surface waters above the thermocline with deeper waters.

The introduction of large amounts of artificial radioactivity into the oceans through nuclear bomb explosions and discharges from atomic reactors has given the marine chemist useful tools with which to intimately study the dissemination of a large number of elements in the marine environment. Although concentration procedures and low-level counting techniques for these radionuclides are often time consuming and difficult, nonetheless, the geochemical behavior of certain previously unstudied elements has become amenable to investigation. Background information on the oceanographic and biological factors that may control the dispersion of the various radioactive species have been adequately considered in several papers (93, 94, 95).

Preliminary investigations with isotopes having half-lives comparable to oceanic mixing processes have been used to study circulatory mechanisms: Sr^{90} (96); Y^{91} , Ce^{144} , Ce^{141} , Ru^{106} , Ru^{103} , Rh^{106} , Zr^{95} , Sr^{90} , Sr^{89} (97, 98); Cs^{137} (99); and Sr^{90} , Sb^{125} , Cs^{137} , Ce^{144} , Pm^{147} (100). Not enough data has as yet been amassed to permit model calculations covering large oceanic areas as in the case of C^{14} .

Several studies have emphasized the enrichment of certain radioactive heavy metals in the marine biosphere (101, 102, 103), and the results are not inconsistent with previous studies on the interaction of organisms with the marine environment (see p. 41).

The three naturally occurring radioactive families of uranium and thorium are characterized in sea water by a lack of radioactive equilibrium within them. This state of affairs, however, has provided a rewarding entry into geochronological and geochemical studies. The parts of the three series investigated are:



The stability of the uranium carbonate complex $\text{UO}_2(\text{CO}_3)_3^{4-}$ gives uranium a relatively high degree of non-reactivity in sea water. On the other hand, less than 2 per cent of the equilibrium amount of Th^{230} , ionium, is found (104, 105); clearly, the thorium isotope is removed by sedimentation processes to the sea floor deposits where it accumulates in high concentrations (106, 107). Further, the Ra^{226} is excessive by sixfold over the amount that could be supported by Th^{230} (104); the radium presumably diffuses into the sea water after its birth from ionium in the sediments. In the U^{235} series, Sackett (108) has found less than 3 per cent of the Pa^{231} that would be expected for a uranium content of 3 $\mu\text{g./l.}$, but observed large amounts of unsupported Pa^{231} in deep-sea deposits. Similar to thorium's behavior, protoactinium is rapidly removed from sea water after its formation.

In the Th^{232} series, the Th^{232} was in excess of the amount presumed to be in radioactive equilibrium with the parent Th^{232} in samples from surface coastal waters in Sweden (104). This unexpected result was interpreted by assuming an excess of the parent Ra^{226} entering these near-shore waters from the rivers. Because of the short half-lives of the daughters of Th^{232} , the disequilibrium between Th^{232} and Th^{232} obviously should exist only in coastal environments. Finally, Ra^{226} appears to exist in amounts larger than its equilibrium value with Th^{232} in deep ocean waters; diffusion of the radium from sediments into sea water is suggested to account for this discrepancy (104).

Stable isotopes.—Deuterium (H^2) concentrations have been found to vary in natural waters by a factor of 25 per cent, with continental waters being lower in this isotope by 0 to 20 per cent (109). Water vapor over oceanic areas is depleted in deuterium relative to the condensed water. With subsequent precipitation from the vapor phases, the rain preferentially accumulates the deuterium, causing the vapor to be further depleted in this isotope. Thus, surface waters of the oceans are enriched in deuterium through evaporation processes resembling a multiple stage fractional distillation (110). The waters H_2O^{16} and H_2O^{18} show similar separation patterns to the corresponding waters H_2O and HDO ; the ratio of the fractionations of each pair is equal to the ratio of the vapor pressure ratios for $\text{H}_2\text{O}^{16}/\text{H}_2\text{O}^{18}$ and $\text{H}_2\text{O}/\text{HDO}$ (111).

In general, equatorial surface waters are enriched in deuterium relative to higher latitude waters; this phenomenon results from the evaporation of large amounts of water from the former sites, with subsequent deposition as rain water near the poles. Surface waters of the ocean tend to be enriched in deuterium relative to the deeper waters, and such differences are attributed to the polar origins of deeper waters (111).

The relative abundances of the boron isotopes B^{10} and B^{11} in sea water differ from an average of 43 terrestrial minerals by an amount that makes marine boron about 2 parts per thousand heavier than the terrestrial material (112).

The isotopic composition of carbon with respect to masses 12 and 13 has been measured in surface and intermediate depth waters of the Atlantic and in one surface sample from the Pacific as well as in marine organisms (113).

The values are given in units of δ in parts per thousand, where

$$\delta = \left(\frac{C^{13}/C^{12} \text{ sample}}{C^{13}/C^{12} \text{ standard}} - 1 \right) 1000$$

and the standard is the Chicago PDB carbon dioxide extracted from a Cretaceous belemnite: sea water, -1 ± 1 ; atmospheric CO_2 , -7 ; organic carbon from marine plants, -7.6 to 16.5 ; calcium carbonate from marine plants, -4.0 to 4.8 ; organic carbon from marine invertebrates, -10.2 to 17.4 ; and calcium carbonate from marine invertebrates, -5.4 to 0.9 . Such results emphasize the rather large extent of the isotopic fractionation of carbon within the marine environment.

The $\text{N}_2^{29,28}/\text{N}_2^{29,28}$ ratio in dissolved nitrogen gas in sea water is altered by the introduction of N_2 produced by the reduction of nitrate ions in anaerobic environments such as the Cariaco Trench in the Caribbean Sea and in Drømsfjord, Norway (114). This biogenic nitrogen gas attained values of 0.5 ml./l. in the more reducing zones of these waters.

Studies on the $\text{O}^{18}/\text{O}^{16}$ ratios in the marine environment have focussed about the water molecules. Surface marine waters, whose salinity ranged between 29 and 40 per thousand, showed variations in the O^{18} content by about 6 per cent (110). Fractionation of these waters followed the pattern of waters containing different hydrogen isotopes (see page 37). The isotopic composition of the dissolved gaseous oxygen has been determined by Rakestraw *et al.* (115) who found that the $\text{O}^{18}/\text{O}^{16}$ ratio was a near mirror image of the content of total dissolved gaseous oxygen with a maximum in the ratio closely coinciding with the oxygen minimum. This fractionation is attributed to a preferential metabolism of O^{16} over O^{18} by marine vegetation, plankton, bacteria, and other sea life.

The $\text{S}^{32}/\text{S}^{34}$ ratio has been observed by a number of investigators to range between 21.75 and 21.90 (116 to 122). It is not possible at present to attribute the range of values of the ratio to isotopic fractionation in nature, or to experimental errors. Trofimov (116) reports the $\text{S}^{34}:\text{S}^{33}:\text{S}^{32}$ as 4.60:0.81:100.

Thode *et al.* (123) have observed a fractionation of sulfur isotopes in the precipitation of sulfides and sulfates in the marine environment, in which the sulfides have been depleted and the sulfates enriched in S^{34} . Their results indicate a striking correlation between geological age and isotopic content, particularly for the sulfides. The activity of autotrophic organisms that oxidize H_2S is apparently responsible for this fractionation. These authors suggest that these organisms became geologically significant at a time around 700 to 800 million years ago. This rather tantalizing hypothesis did not find confirmation in subsequent Russian work (124) in which no age correlation was found for the isotopic sulfur composition of 47 pyrite and sulfate samples.

Owen & Schaeffer (125) give a value of 3.142 for the $\text{Cl}^{35}/\text{Cl}^{37}$ ratio in Atlantic Ocean samples. This value was the same, within experimental errors, as the ratios from a suite of igneous and sedimentary minerals. Similarly, the $\text{Br}^{79}/\text{Br}^{81}$ ratio in sea water of 1.0248 ± 0.001 is similar to that of terrestrial materials (126).

The isotopic composition of strontium in sea water has been determined (127): $\text{Sr}^{86}/\text{Sr}^{88} \times 10^4 = 1195 \pm 4$ and $\text{Sr}^{87}/\text{Sr}^{88} \times 10^3 = 718 \pm 3$. Gast (128) finds that the Sr^{87} abundance in marine calcareous shells and sea water from the mid-Atlantic ocean did not vary by more than 0.35 per cent in strontium isolates.

CHEMICAL REACTIONS IN THE OCEANS

Three general and complimentary approaches to an elucidation of the chemical reactions occurring in the oceans have been fruitful in recent investigations: the relative reactivities of the elements and the nature of their environment; the composition of the end-products; and, finally, the spatial and temporal distribution of the reactants and products.

A chemical reaction that is extensive enough to influence or possibly control the concentration of some elements in sea water is of primary concern. The life processes have long been known to be responsible for the most dramatic compositional changes and for the regulation of abundances of many elements (2). Insight into inorganic reactions of major importance has been enhanced by considerations of the relative reactivities of elements on the basis of the average time an element spends in the oceans. A drastically oversimplified model assumes only one oceanic domain and that the presently observed chemical composition reflects a steady state system in which the amount of material introduced per unit time is compensated by an equal amount deposited as sediments. A further assumption is that there occurs a complete mixing of a given element in the oceans during times that are short with respect to the element's life in the oceans. We can then define and calculate the residence time of an element as the total amount of the element in sea water, divided by the amount introduced by the rivers or precipitated to the sediments, per unit time. Barth (129) used the river influx and Goldberg & Arrhenius (16) the sediment deposition in computations, and a remarkable agreement is observed between the two sets of data.

At the high end of the spectrum of residence times are the alkali metals and alkaline earths with values between 10^6 and 10^8 years indicating a relative lack of reactivity which is in accord with their marine chemistries. Al, Fe, and Ti are among the elements with the shortest residence times (10^2 to 10^3 years). Such elements enter the oceans in part as solid phases such as feldspars, clay minerals, and hydroxides of iron that rapidly settle to the sea floor. The absolute values of their residence times are somewhat tenuous because the assumption that such times are large (in comparison with mixing times of oceanic water masses), say of the order of hundreds to thousands of years, is not satisfied.

Manganese (7000 years) has an intermediate value along with certain other metals such as zinc (180,000 years), cobalt (18,000 years), and copper (65,000 years). The reactivities of these elements are clearly connected with the formation of ferromanganese minerals which have a widespread distribution in all oceans. Menard & Shipek (130) estimate that they cover between 20 and 50 per cent of the sea floor in the Southwestern Pacific. Structural

investigations by Buser & Grütter (131) indicate that the minerals are composed of δ - MnO_2 , manganites and goethite, as well as some amorphous fractions. δ - MnO_2 is formed of disordered sheets of manganese dioxide, whereas the manganite crystals possess a double-layer-lattice structure in which ordered layers of manganese dioxide alternate with disordered layers of manganous or ferric hydroxides or basic salts. The disordered layer is the site for the accumulation of such metal ions as zinc, cobalt, and copper. These guest metals, which are highly enriched in the ferromanganese minerals as well as the manganese, exist in states of undersaturation, and their role in the formation of these minerals has been postulated to account at least partially for this situation (132). Their higher residence times, compared to manganese, reflect the larger amounts of manganese in these materials: Mn, 19 per cent; Zn, 0.04 per cent; Co, 0.3 per cent, and Cu, 0.5 per cent (133).

The reaction, $2 \text{OH}^- + \text{Mn}^{++} + \frac{1}{2} \text{O}_2 = \text{MnO}_2 + \text{H}_2\text{O}$, has a free energy of -9 kcal. at a pH of 8, a manganous ion concentration of $10^{-9} M$, and a partial pressure of oxygen of 0.25 atm., values characteristic of sea water at the sediment-water interface. Since tetravalent manganese is not found in sea water, although from the above data it is the thermodynamically stable form, a reaction site or surface is probably necessary for the reaction to proceed. The well-known catalytic properties of iron oxide surfaces suggest the association of the material in the formation of the nodules. Iron exists in sea water dominantly in particulate phases, partly colloidal. The accumulation of iron oxides on surfaces where either the bottom topography or the lack of sediment source material does not allow any appreciable accumulation of solid phases would initiate the formation of the ferromanganese minerals. In areas of rapid deposition, where nodules or accretions of these materials are not found, the burial of any iron oxide surface by the other sediment components minimizes any mineral formation (133). The rates of formation of these minerals are of the order of atomic layers per day (16).

The conditions under which minerals form in the ocean system can be interpreted through their chemical or isotopic compositions. For example, although thermodynamic data for marine carbonate-fluorapatites, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_{2-3}$, do not exist, the character of the environment in which they form can be ascertained. These phosphates contain uranium in concentrations from several thousandths to several hundredths of 1 per cent; this uranium exists in the tetravalent state from a few to more than 90 per cent of its total content (134). Experimental evidence indicates that the tetravalent uranium occurs as a structural replacement for calcium (134), while the pH and redox potentials of sea water permit only the existence of uranyl ion, primarily complexed as the carbonate (135). The conditions for marine apatite formation thus require an environment capable of reducing $\text{UO}_2(\text{CO}_3)_3^{-4}$ to U^{+4} . These minerals occur in coastal deposits where, in the overlying waters, high production of organic matter takes place which in part accumulates at the sediment-water interface (136). The combustion of these biological materials results in a complete utilization of the dissolved

oxygen at the reaction site, thus producing the required reducing conditions (137).

The observations that the concentration of heavy metals is greater in the marine biosphere than in the hydrosphere have been complimented by a series of investigations emphasizing the remarkable specificity of certain organisms. It has long been known that certain ascidians contain organically bound vanadium to levels of 6500 p.p.m. by dry weight. Recently, Carlisle (138) investigated the concentration of niobium in this group of organisms and found contents of this element up to 75 p.p.m. He noted that, with species containing either niobium or vanadium, those having vanadium contained no detectable niobium and, conversely, those with detectable niobium held only traces of vanadium. These enrichments occurred in sea waters with vanadium and niobium contents of 4×10^{-8} and 10^{-10} molar respectively.

The analyses of Curl *et al.* (139) on a group of zooplankton emphasized specificity in their enrichments: lead in copepods, cadmium in squids, molybdenum in crustaceans, and cobalt in chaetognaths. Further, the strikingly high contents of lead (65 to 200 p.p.m. in the ash) and vanadium (16 to 85 p.p.m. in the ash) in pteropod shells could be a major pathway for the removal of these elements from sea water. The results led the investigators to suggest that "for any given chemical there will be found at least one planktonic species capable of spectacularly concentrating it."

The relative concentration factors of metals in the marine biosphere as compared to sea water closely parallel the order of stability of complexes formed between metal ions with a variety of organic ligands (28). Schubert (140) has found the general order of increasing stability for divalent ions (essentially independent of whether the attachments of the metal are to oxygen, nitrogen, or sulfur atoms) as: $\text{Pd} > \text{Cu} > \text{Ni} > \text{Pb} > \text{Co} > \text{Zn} > \text{Fe} > \text{Cd} > \text{Mn} > \text{Mg} > \text{Ca} > \text{Sr} > \text{Ba} > \text{Ra}$. This can be compared, for example, with the fractionation factors for sponges (141): Cu, 1400; Ni, 420; Co, 50; Mg, 0.07; and Ca, 3.5. Thus, the animals and plants of the sea can be considered a huge reaction area for the uptake of dissolved metallic ions, with the governing factor for the retention of a specific ion in competition with other ions as the equilibrium constants of the complexing reactions.

The chemical, isotopic, and mineralogical compositions of calcium carbonates found within sea waters not only maintain a record of the environmental parameters but also are indicative of whether the precipitation was biological or inorganic. On the basis of $\text{C}^{13}/\text{C}^{12}$ and $\text{O}^{18}/\text{O}^{16}$ ratios, Lowenstam & Epstein (142) concluded the marine calcareous oolites are of inorganic origin while the sedimentary aragonite needles are apparently derived from algal carbonates in samples from the Great Bahama Bank area. Further, the uranium and strontium contents of oolites compare favorably with values found in a laboratory precipitation but differ markedly from values in calcareous materials of an organic origin (with the exception of the corals) (143, 144).

Chemical reactions occurring within the upper levels of the oceans are associated with either the primary production of plant material by photoautotrophic phytoplankton or the subsequent combustion of organic matter. The reader is referred to an exhaustive review on marine productivity by Nielsen (145). The seasonal character of plant production and the subsequent oxidation processes result in both spatial and temporal changes in the concentrations of the chemical reactants and products.

Considerations of the reactions in zones below the photosynthetic layers where the dissolved oxygen gas has been completely depleted, or very nearly so, have resulted in several new concepts. These oceanic areas are highly productive, with the associated loss of oxygen due to the remineralization of sinking organic materials. In the anaerobic waters of the Black Sea the production of hydrogen sulfide has been shown to accompany the loss of sulfate, thus establishing the principal origin of the sulfide sulfur as the reduction of sulfate rather than as the decomposition of organic matter (146, 147). Nitrite ion accumulates below the photosynthetic zone following the oxidation of ammonia released from decaying organic phases. In the highly productive areas of the Eastern Tropical Pacific, Brandhorst (148) observed a second maximum in nitrite concentration in deeper waters where the dissolved oxygen gas was 0.1 ml./l. or less, and he attributed this nitrite to the reduction of nitrate by denitrifying bacteria. Gaseous nitrogen, produced from the reduction of nitrate, has been observed in deep waters of the Black Sea (149), Cariaco Trench (114), and Dramsfjord (114).

The search for an index of organic productivity that becomes incorporated as a component in the sedimentary deposits has centered around barium. The transfer of barium from surface to deep waters by organisms or the combustion of organic phases can result in barium sulfate precipitating at or near the sea floor (32). Hence, the rate of barium accumulation in the sediments should reflect the amount of biological activity in the overlying waters. Goldberg & Arrhenius (16) found rates of barium accumulation to be more than twenty times higher under the high productivity zones of the equatorial divergence than in areas to both the north and south in the Pacific Ocean. Further, marked variations in the time of organic productivity are paralleled by concentration changes of barium, although post depositional migration of barium in the sediments appears to destroy the record for times greater than 200,000 years. The sediments considered in this work contained appreciable amounts of calcium carbonate of a biological origin. Barium was co-variant with the content of biological siliceous remains (opal) in a pair of cores from the Bering Sea (150); the rate of accumulation of opal was presumed associated with the productivity.

RATES OF SEDIMENTATION

Studies on the rates of sedimentation on the deep-sea floor have been concerned primarily with the Pleistocene era inasmuch as the majority of cores have penetrated materials deposited up to or into the Tertiary.

Carbon-14 measurements on the calcareous foraminiferal components of

marine sediments have offered promise for rates-of-accumulation studies, but so far only a few investigations have been carried out. Arrhenius *et al.* (151) determined the sedimentation rates in some cores from the Eastern Equatorial Pacific using the C^{14}/C^{12} ratios with the assumption of a constant rate of clay accumulation. This assumption was not confirmed in the subsequent work of Broecker *et al.* (152) who made rather extensive measurements of the C^{14}/C^{12} ratio in an Equatorial Atlantic core. These workers found that the sedimentation rate of the non-calcareous components approximately quadrupled and that of the carbonate phases doubled during the glacial period. The change from lower to higher rates occurred about 11,000 years ago.

Attempts at establishing geochronologies in marine sediments for periods up to a half-million years have depended primarily upon dis-equilibrium in the natural uranium and thorium radioactive series. The ionium-radium method, based upon the removal of ionium from sea water soon after its formation and upon the subsequent growth of radium in the sediment, has produced questionable results. Migration of the daughter radium from its parent ionium in the deposit site and the non-uniform deposition of ionium with time have nullified many of the derived ages (153, 154). Picciotto & Wilgain (155) proposed the ionium/thorium method which assumes the simultaneous removal of the ionium and Th^{232} from sea water to the sedimentary deposits. Rates of accumulation through about the last half-million years are potentially obtainable, i.e. approximately five half-lives of ionium ($t_{1/2} = 80,000$ years). A number of assumptions govern the validity of the method: the Io/Th ratio in the waters overlying the sediment have to remain constant over the time intervals to be measured; the ionium and thorium must be in the same chemical forms in sea water; the analyzed materials from the sediments can't contain any detrital materials that contain significant amounts of either of these isotopes of thorium. The initial applications of the technique indicate that the results are compatible with the above assumptions (106 to 108; 156 to 160). The Russian investigators (107, 157, 158) found, in bottom samples from the Pacific and Indian Oceans, that the ionium was almost completely supported by uranium in near-coastal deposits, but in areas distant from the coast there can be one to two orders of magnitude more uranium-unsupported than uranium-supported ionium. The value of the ratio in surface samples is systematically related to the collecting sites (106, 156). Apparently, sea water thorium isotopes are incompletely mixed in pelagic areas.

Barnes *et al.* (161) have used the growth of ionium from its parent uranium to determine the rates of accumulation of marine coral deposits. This method is based upon the apparently valid assumption that the newly deposited corals are essentially free of ionium. This technique was successfully extended to calcareous oolites that deposit inorganically from sea water (143).

EVOLUTION OF THE OCEANS

The chemical compositions, volumes, and sources of the chemical species of the oceans as a function of geologic time are fundamental to many prob-

lems in earth science, yet an unambiguous history of the marine environment is lacking at the present time. Two general types of hypotheses on the evolution of the oceans and atmosphere have been proposed: (a) that they have accreted continuously, though not necessarily uniformly, through geologic time; and (b) that these two geospheres are residual from a primitive atmosphere that surrounded the earth.

Rubey (162, 163) has thoughtfully gathered together much of the pertinent evidences bearing on these problems and concludes that the oceans and atmospheres have evolved gradually. He points out that the water, as well as such elements as C, N, B, S, Cl, Br, and I, are much too abundant in the hydrosphere, atmosphere, and biosphere to have been derived from the weathering of crustal rocks as were the cationic species in the oceans. Calculations on the amounts of these materials necessary to produce the present day oceans and atmosphere indicate that the most probable sources are the materials in gases escaping from volcanoes, fumaroles, and hot springs, and the gases occluded in igneous rocks. He suggests that such materials were released from intrusive and extrusive rocks that have continuously risen from the deep interior of the earth.

Urey (164) classifies those elements that would concentrate at the earth's surface into two groups on the basis of the chemical and physical properties of their most probable states during their passage from the interior: those that rose to the surface as a result of their volatility (H_2O , C as CH_4 or CO_2 , and N as N_2 or NH_3); and those that were transferred in solution at temperatures of $100^\circ C$. or less (Cl, Br, B, and possibly I).

Rubey (162, 163) indicates that the composition of the oceans could have varied only within relatively narrow limits during past ages. Lowenstam (165), on the basis of O^{18}/O^{16} and Sr/Ca ratios and the $MgCO_3$ contents in fossil brachiopods from times as far back as the Mississippian, asserts that these elemental and isotopic abundances must have remained essentially constant during the last 2.5×10^8 years.

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PHYSICAL PROPERTIES OF HIGH POLYMERS^{1,2}

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This report is concerned principally with studies of molecular motion, structure, and structural changes in polymers. The present stage of knowledge of physical properties of high polymers will be presented mainly with reference to the literature of the last two years. The great number of published investigations necessitates restriction of this discussion to the fundamental problems.

MOLECULAR MOBILITY IN POLYMERS

In recent years two techniques were developed that applied to the study of the processes of molecular motion. These are nuclear magnetic resonance and the investigation of relaxation processes with the help of mechanical or dielectric methods (relaxation spectrometry).

The basis of nuclear magnetic resonance absorption has been discussed in detail in a number of papers (1, 2, 3). Here we will consider only a few points important for the investigation of high polymers. Along with mass and charge, another characteristic of the atomic nucleus is its spin, which can be integral, half-integral, or zero. If the nuclear spin is different from zero, it can assume only certain quantized angles of inclination in an external magnetic field. By means of a weak electromagnetic radiation field, these angles of inclination can be changed according to the laws of quantum mechanics. This effect is accompanied by absorption of energy from the radiation field and can be detected by electronic means. Almost always the graphic record of this energy absorption is obtained as an absorption line, which, with constant radiation frequency, depends upon the magnetic field in the neighborhood of the individual nuclear spin. Since, however, every atomic nucleus with a non-zero spin is itself the source of a magnetic field, the frequency of the absorption line is determined not only by the external magnetic field, but also by the field caused by the neighboring atomic nuclei. Because of this interaction between the magnetic moments, the energy absorption of the total system is spread over a more or less wide field, or frequency range. If the relative positions of the atomic nuclei remain unchanged because of the absence of molecular motion, a broad absorption line of several gauss occurs. If, however, the relative positions of the atomic nuclei change through more or less strong molecular motion, the magnetic interaction is weakened, and an absorption line having changed in form and width is observed.

Bloembergen, Purcell & Pound (4) and Gutowsky & Pake (5) have shown

¹ The survey of literature pertaining to this review was concluded in October, 1960.

² The following abbreviations are used: Hz (Hertz, or cycle per second); kHz (kilo-Hertz); MHz (Mega-Hertz).

that the line width is a suitable measure of mobility and have sufficiently explained the phenomenon of "restriction of motion." However, in order to discuss the structure of the molecule and the form of the motion, it is necessary to determine the second (or even fourth) moment of the absorption line. The theoretical basis for this has been given by van Vleck (6) for the rigid lattice model. These quantities should, theoretically, be independent of the temperature. Andrew & Newing (7) have shown how the experimentally observed temperature dependence of the second moment may be understood. In several papers Miyake and others (8 to 14) have tried to interpret and understand the experimental results obtained for a number of high polymers.

The application of mechanical and dielectric methods to the investigation of molecular motion, on the contrary, is based solely upon the fact that thermal molecular motion is always present above the absolute zero of temperature. The spatial rearrangements, arising from this thermal agitation, are strongly temperature dependent. Because of the complex structure of high polymers, different types of spatial rearrangement can take place simultaneously but with different probabilities. At lower temperature, the small molecular units, such as CH_2 or CH_3 groups, come into motion (15, 16). At higher temperatures the somewhat larger molecular units, e.g., side groups, follow, and finally, above T_g , micro-Brownian motion (segmental motion) is freed. Above this temperature, which marks the transition from the non-equilibrium state of the glass to the state of inner equilibrium (the melt), cooperative rearrangement involving neighboring monomer units, whose number has been estimated at 10 to 30, becomes possible. With noncross-linked amorphous polymers, the micro-Brownian motion is converted into macro-Brownian motion (e.g., self-diffusion melt viscosity). With crosslinked polymers this process cannot take place without the destruction of the network, and in the case of partially crystalline polymers, macro-Brownian motion becomes important only above the melting point.

If the material is left to itself, spatial rearrangement can take place in all directions of space with equal probability. If, however, a mechanical or electrical field is imposed, the molecular motion obtains a preferred direction such that the stresses brought into being by the external field are removed as quickly as possible. This process is not instantaneous, however, but delayed (relaxation). The experimental method of relaxation spectrometry, which detects such molecular motion, may be carried out in both mechanical and electrical cases under either static or dynamic conditions.

In the static experiment one observes the sample's reaction with time after momentary application of the external field. The processes of molecular motion become apparent as a decrease with time of the elasticity modulus, or of the dielectric constant or conductivity, as the case may be.

In the dynamic experiment the frequency dependence of the complex dynamic elasticity modulus (or complex dielectric constant) is measured. The introduction of the complex quantities recognizes that a phase shift appears between the external stress and the deformation (or current). The re-

sults of the static and dynamic methods may be interconverted with the help of the linear relaxation theory (17). The relaxation time spectrum and the Williams-Landel-Ferry equation (18), that is, the temperature dependence of the apparent activation energy, have proved sufficient for a complete description of the linear viscoelastic behavior of many polymers above T_g . The determination of these functions requires measurements over a sufficiently large time and temperature range. For a summary of work done in past years the reader is especially referred to (19 to 31). In this report only more recent, selected results of the years 1959 and 1960 will be presented and discussed in so far as they are known to the authors. References will be made to earlier work only when necessary.

POLYSTYRENE

Cox, Isaksen & Merz (32) have reported on an independent method of determining the number average molecular weight \bar{M}_n of polystyrene in the solid state. With a torsion pendulum they determined the temperature dependence of the logarithmic decrement above the glass temperature T_g of polystyrenes made by various methods for which the molecular weight and molecular weight distributions were known. With increasing temperature the logarithmic decrement decreases at first, since the tangling of the macromolecules sets up a sort of network, which, however, disappears again with further increase in temperature. The damping increases again. The smallest value of the logarithmic decrement is a simple function of \bar{M}_n .

McCormick, Brower & Kin (33) investigated the influence of the molecular weight distribution on various properties of polystyrene (tensile strength, tensile modulus, elongation, tensile impact strength, and heat distortion). The dependence of these quantities on the various types of molecular weight average is discussed. The effect of the chemical structure on the softening point for 25 different substituted polystyrenes has been investigated by Barb (34) by a conventional method (horizontal cantilever bending test). As expected, he finds that an elevation of the softening point may be brought about by (a) stiffening of the principal chains, (b) intramolecular steric hindrance (e.g., *ortho*-substitution), (c) increasing intermolecular hindrance [e.g., in poly-(methyl styrene)], and (d) dipole interaction. The rise in the glass temperature of polystyrene brought about by *p*-substitution of fluorine, chlorine, bromine, and iodine apparently has no fundamental relationship to the dipole moment of the substituent, as was shown by Illers (35) through mechanical damping measurements and by Kosfeld (36) through nuclear magnetic resonance measurements. A practically linear relationship is found between the effective volume (atomic volume) of the substituent and the rise in the glass temperature ΔT_g (with reference to the glass temperature of unsubstituted polystyrene (36)). It must, therefore, be concluded that intermolecular steric hindrance is the important factor in the rise of the glass temperature in *p*-substituted polystyrenes. Investigation of the secondary dispersion region at 330°K., which was found by dynamic-mechanical measurements (37), was carried out by Kosfeld (36) with the help of nuclear magnetic reso-

nance measurements. It was shown that the damping observed in the dynamic-mechanical experiment could be attributed to a very small turning of the benzene nucleus. This effect can be clearly observed through the variation of the second moment with the temperature (36, 38).

Wall, Sauer & Woodward (39) investigated the dynamic-mechanical behavior of atactic and isotactic polystyrene in a temperature range between 80 and 500°K. at frequencies between 200 and 2500 Hertz. Except for the familiar α -loss maximum at 400°K., no further relaxation process was found in the temperature range investigated. Nevertheless, below 200°K. a rise in the loss factor is observed that is more prominent with atactic than with isotactic polystyrene. This point was more closely investigated by Illers & Jenckel (40) by means of torsion pendulum measurements on linear and crosslinked polystyrene, poly-*p*-chlorostyrene, and poly-*p*-bromostyrene in the temperature range between 100 and 220°K. In all of these polymers a maximum in the damping (γ -maximum) is found between 130 and 150°K. This is ascribed to the molecular motion of two consecutively placed CH₂-groups that arises now and then through head to head polymerization and corresponds to the analogous processes in polyethylene, polyamides, and higher poly-*n*-alkyl-methacrylates in the same temperature range.

The photoelastic properties of various substituted polystyrenes with α -methyl styrene, methyl methacrylates, and acrylates in the glassy state were the object of an investigation by Rudd & Andrews (41). The results indicate that steric effects, especially in the neighborhood of the principal chain, influence greatly the nature of the molecular mobility during distortion in the glass state. An α -substitution on the chain or an *o*-substitution on the phenyl nucleus cause a stronger hindrance than a *p*-substitution on the phenyl ring. Kosfeld (38) reaches similar conclusions in the discussion of the second moments obtained from nuclear magnetic resonance measurements [see also (34)].

Nuclear magnetic resonance studies on plasticized polystyrenes (42) have indicated that, in the glassy state of the system, the solvent has high molecular mobility (similar to a liquid) even up to around 50–60°K. below the corresponding glass temperature. The number of quasi-freely moving solvent molecules decreases with an increased temperature difference between the temperature of the system under consideration and its glass temperature. Until recently the resolution of relaxation curves into a continuous distribution of relaxation times was possible only by approximation methods for amorphous polymers. Tobolsky & Murakami (43) suggest a method by which, in favorable cases, the relaxation modulus in the rubber-like flow region can be resolved into a discrete relaxation time distribution. This method yields sufficiently accurate values for at least the two highest relaxation times when applied to mono- and polydisperse polystyrenes.

POLY-*n*-ALKYL-METHACRYLATE POLYMERS

Ferry and associates are continuing their investigation of the dynamic-mechanical properties of poly-*n*-alkyl-methacrylates. By means of a torsion

pendulum described by Plazek, Vranken & Berge (44) and by creep experiments, they can expand the frequency range of their double transducer method to longer times. Solutions of poly-*n*-butylmethacrylates in diethyl phthalate (45), poly-*n*-octylmethacrylate (46), poly-*n*-dodecyl methacrylate (47), and poly-*n*-docosyl methacrylate (48) are being studied. The anomalies that appear through the use of a time-temperature superposition are explained either by the tendency to crystallization evident for the side groups in the case of the higher esters, or as the separation of the tangling points with increasing temperature. A new method of superposition is suggested that takes account of this fact. Low frequency measurements made by Koppelman (49) on polymethyl methacrylate in the region between 10^{-4} and 10^{-1} Hertz and from 190 to 420°K. show that the Poisson constant in the glassy state is independent of the temperature 0.30. Heijboer (50) continued his interesting experiments on polymers containing cyclohexyl groups. By means of dynamic-mechanical and dielectric methods, the motion of the cyclohexyl groups is found to be practically independent of the molecular environment, while analogous relaxation processes of the dioxane ring are more strongly dependent upon environment. The molecular mechanism is the transformation of the groups between the two chair forms, and arises only when these are not identical. Sinnott (51) is making measurements of the shear modulus and of internal friction with a torsion pendulum in the region between 4.2 and 100°K. and with a frequency of about 10 Hertz on polymethyl- and polyethylmethacrylate. The ethyl polymer shows a damping maximum at 41°K. that is absent with the polymethylmethacrylate. Since the reorientation of the ester-*n*-alkyl groups occurs at higher temperatures as the ester group increases in size, Sinnott supposes that the relaxation process takes place below 4.2°K. in the latter polymers. Using nuclear magnetic resonance measurements in the temperature region between 77 and 400°K., Sinnott shows (52) that the motion of the methyl and the ethyl of the ester group in the polymethacrylate and the polymethylmethacrylate, as well as the polyethylmethacrylate, sets in below 77°K. and that the motion of the methyl group of the principal chain in the polymethylmethacrylate sets in above 130°K. This result is in agreement with mechanical and dielectric measurements. The experimental results are supported by theoretical considerations and calculations. Slichter & Mandell (25) have also carried out nuclear magnetic resonance measurements on polymethacrylate and polyethylmethacrylate. The results of these authors are in basic agreement with those of Sinnott.

Herwig & Jenckel (53) investigated the direct current behavior of polyvinylacetate and polymethacrylate under variation of electrical potential, temperature, and previous electrical and thermal history. They show that the nonstationary passage of current depends on a reversible polarization process, while the stationary current passage depends on ion conductance. Further, the authors calculate, from direct current measurements, frequency and temperature dependent values for ϵ'' in the region from $10^0 < \omega < 10^{-6}$ Hertz. These results coordinate well with measurements of alternating cur-

rent loss at higher frequencies. With the help of molecular physical considerations, conclusions are drawn as to the conductance and polarization mechanism. Finally, the reader is referred to a paper by Beevers & White (54), which discusses the dependence of the glass temperature on the molecular weight for polymethylmethacrylate. Their results can be well accounted for by earlier theories (55, 56).

POLYVINYLCHLORIDE

A detailed study by Sommer (57) concerns itself with the elastic behavior of polyvinylchloride under static and dynamic stress. With the help of static and dynamic methods, the complex (or, respectively, the time-dependent) elasticity modulus was experimentally studied in the range of the glass temperature T_g (190–390°K.) and using a time-scale ranging from 10^{-4} to 10^{+5} sec. The phenomenological description of the results, with the help of the relaxation time spectrum, leads to the conclusion that the discrepancies between the static and the dynamic experimental results come about because of differences in entropy of activation. It appears that the mutual inter-conversion of static and dynamic results cannot be rigorously carried out for this material. Using a spring-dashpot model, Becker (58) has discussed the relationships between the elastic moduli determined by static and dynamic means and has checked the results through measurements of the relaxation or creep behavior of slightly plasticized polyvinylchloride. The approximate formulae that he developed allow a sufficiently exact description of the behavior of the material.

The experimental determination of the complex dielectric constant was carried out by Ishida (59, 60) in the temperature range between 110 and 390°K. and at frequencies between 100 Hz and 2 MHz. This investigation includes not only the α -relaxation process, which depends upon segmental motion, but also the β -process, which occurs at lower temperatures (or higher frequencies). The parameters of the Cole-Cole circular arc law (61) change with the temperature in different ways for the two processes. This variation in behavior is related to the glass temperature (59). In order to clarify the molecular cause of the β -process, Ishida (62) has carried out measurements of the dielectric constant of three polyvinylchloride fractions with degrees of polymerization of 200, 1000, and 1400 at constant temperature. It was found that the β -absorption is not related to the end groups, as Reddish (63) has assumed, since the Cole-Cole parameter for the absorption does not change. Ishida (62) considered that the β -absorption will be due to small displacements of the dipoles near the frozen-in position.

Similar dielectric studies were carried out on a co-polymer of vinyl chloride and vinylidene chloride (as well as on polystyrene, polymethylmethacrylate, polyvinylacetate, polyethylenterephthalate, and polyacrylonitrile) by Saito & Nakajima (64) under static and dynamic experimental conditions and in the region between 10^{-4} and 10^6 Hz, which includes spatial rearrangement resulting from segmental motion. In connection with measurement of

the volume as a function of temperature and time, which was undertaken simultaneously with these polymers, the results are so interpreted that a glass transition takes place in the case of the amorphous polymers, while a thermodynamic transition is supposed with partially crystalline polymers. The arguments given, however, are not convincing. Specifically, the dielectric measurements are not continued to sufficiently low temperatures with the amorphous polymers. Because the volume of the partially crystalline copolymers of vinyl chloride and vinylidene chloride has already reached a constant value after 600 min. at a temperature 10° under the glass temperature T_g , one cannot conclude the presence of an equilibrium state. Particularly with partially crystalline systems, hindrance of the volume after-effect of the amorphous regions by the crystalline regions may take place.

POLYAMIDES AND POLYURETHANE

A great number of recent papers are concerned with motion in polyamides. Here, good progress has been made with regard to understanding the physical and technological properties on a molecular basis. These polymers, which are built up of a regular succession of polar carboxylic amido-groups and nonpolar methylene chains and are usually partially crystallized, are distinguished by the fact that intermolecular hydrogen bridges exist between the NH- and CO-groups of neighboring molecules that probably are completely formed not only in the crystalline but also in the amorphous regions (65). Water molecules dissolved in polymers are known to break up these hydrogen bridges and probably enter into specific interaction with the carbonyl groups of the polyamides. The changes in physical properties that are expected because of this are the object of a great many studies.

All polyamides thus far studied exhibit three relaxation processes in the temperature zone between 90°K. and the melting point of the crystalline regions, provided that the polymers have not been carefully dried. The mean temperatures for these processes are at about 310 to 330°K. (α' -process), 200°K. (β' -process), and 120°K. (γ -process) for a testing time of 1 sec. The α' -process occurring in the neighborhood of 320°K. corresponds to the glassy solidification of the amorphous regions below the glass temperature T_g . The molecular process, here leading to a maximum in the frequency or temperature dependence of the mechanical or dielectrical loss factor in dynamic experiments, is one of cooperative rearrangement of chain segments. This is the same molecular process that is frozen-in during the transition from the equilibrium melt to the glass. The static and dynamic Young's or shear modulus exhibits a sharp decline with increasing temperature or decreasing frequency, and the analogue effects hold true for the dielectric constant and the electrical conductivity.

Quistwater & Dunell (66, 67, 68) have studied the dynamic tension modulus and energy loss for nylon 6,6 monofilaments in the region of the α' -process at 282°K. , 308°K. , and 333°K. over a wide range of relative humidity (10 to 90 per cent) under forced longitudinal vibration (10 to 30 Hz)

and have discussed a time-humidity superposition method analogous to the time-temperature reduction method of Ferry and Tobolsky. At 308 and 333°K. it is possible to superimpose the curves measured at different values of relative humidity on a master curve having the same displacement constants for E' and E'' . At 282°K. this method fails, probably because at this temperature the transition from the glass to the equilibrium state takes place with progressive sorption of water.

Woodward, Crissman & Sauer (69), as well as Illers (65), have studied the softening effect of water on the α' -relaxation process at frequencies of around 1000 Hz and 1 Hz. According to Woodward and others, who also studied the influence of an N-methylation of the carboxyl amido-group, the lowering of the mechanical principal-loss maximum comes about through the diminution of the intermolecular interaction as caused by sorbed water breaking up the hydrogen bond. Glick *et al.* (71) arrive at similar results through nuclear magnetic resonance measurements on deuterated and non-deuterated nylon 6,6, dried and 47 per cent crystalline. Woodward, Glick, Sauer & Gupta (72) find good agreement between dynamic-mechanical and nuclear magnetic resonance measurements with various polyamides. The transitions comprehended in the dynamic-mechanical experiment occur at the same temperature in the half-value width curve and in the second moment. A more exact analysis of the experimental data, nevertheless, shows that the steps in the second moment occur at somewhat higher temperatures than do the steps in the modulus corresponding to the same molecular processes. This might be attributed to a superposition of processes that occur in the amorphous and the crystalline regions preceding melting. The fact that water has a different influence on the amorphous and the crystalline regions makes it appear possible that the transition occurring in the second moment may be caused by two separate processes of molecular motion.

According to Illers (65) the great influence of very small weight percentages of water on the glass temperature can be explained by the proposition that the water molecules themselves form hydrogen bridges to the carbonyl groups. Similar studies by Illers (70) on 6,6- and 6,12-polyamides using methyl ethyl, propyl, and butyl alcohols shows that the softening effect of the alcohols decreases in the above order if weight per cent is chosen as the measure of concentration. However, a common curve results for all polyamides and alcohols if one plots the temperature of the mechanical α' -maximum against the mole fraction of the alcohol in the amorphous regions. With 6-nylon and polyurethane it was determined that polar and polarizable solvents (as, for example, acetone, CH_2Cl_2 , C_6H_6 , C_6H_{12}) behave similarly to the alcohols and water (73). It is interesting that with mole fraction as concentration variable the softening effect of all the alcohols was considerably stronger than that of the water.

Boyd (74) has carried out dielectric studies on 6,6-nylon over a large frequency range. Radiation crosslinking, as well as the effect of dissolved water, methyl and ethyl alcohol was studied. Application of a theory of

Fuoss & Kirkwood (75) shows that above T_g the relaxation time distribution is temperature dependent at all concentrations, so that no time-temperature reduction method can be used. It follows also from these studies that the water is relatively tightly bound to the carboxyl amido groups. Dielectric measurements were made by McCall & Anderson on six different polyamides (77). The results agree with the studies of Boyd (74). These authors conclude from direct current measurements that the amido protons in the amorphous regions contribute importantly to ionic conductance. At high frequencies and suitably high temperatures the dipole relaxation of the amido groups in the amorphous regions is the important mechanism of motion. This interpretation is supported by the occurrence of a sharp step in the line width in nuclear magnetic resonance experiments (between 320 and 370°K.).

Kawaguchi reports on the physical properties of 18 polyamides (76). The measurements, carried out at frequencies of around 100 Hz over a large temperature range, were done on samples of unknown degree of crystallization and water content, making a comparison with other measurements impossible. Bobalek, Lacson & Dawson (78) have studied the changes brought about in the mechanical properties of 6,6-nylon, 6,10-nylon, and 6-nylon in the neighborhood of the α -process by steam or heat treatment, and they found that these changes were reflected in the micro-structure of the fractured surface when the samples were broken at 239°K.

A very interesting paper concerning the dynamic-mechanical properties of graft co-polymers of 6,6-nylon in a torsion pendulum experiment was published by Shinohara (79). Methylmethacrylate, acrylic acid, acrylonitrile, vinyl acetate, methyl acrylate, and ethyl acrylate were grafted onto the nylon through radiation. As is to be expected, two α -maxima occur that lie at about the same temperatures as those of the corresponding homopolymers. The changes in the intensities of these two relaxation processes are discussed. In this respect, it might be noted that it is physically more correct to discuss these changes, not with respect to the quantity $tg\delta$ which contains both the reversible and irreversible effects, but rather with respect to the imaginary part of the complex modulus (E'' , G'') or, respectively, the complex dielectric constant. This was shown by Illers & Kosfeld (80) with the dynamic-mechanical behavior of a 6,12-polyamide in the temperature range between the glass temperature and the melting point. An increase in the temperature dependence of $tg\delta$ in the temperature range below the melting temperature (designated in the literature as the α -maximum) does not occur in the temperature dependence of G'' . This increase, therefore, is not attributable to a new relaxation process.

The β -relaxation process was investigated by means of dynamic-mechanical methods by Woodward, Crissman & Sauer (69), Kawaguchi (76), Dunell, Joanes & Rye (81), Illers (65) and Jacobs (73). This process is not present in carefully dried polymers, but appears only after addition of water, alcohols, and other low molecular weight liquids (65, 69, 70). The molecular mechanism is, according to some (69, 76), a rearrangement of those parts of the chain

that are not bound by hydrogen bridges. Contradicting this conclusion, however, is the fact, among other things, that this process is not present in N-methylated polyamides (69). Illers (65) attributes this process to rotational rearrangement of solvent molecules that are bound to the carboxyl amido-groups. Dunell, Joanes & Rye (81) attempt a phenomenological description of the β -process by applying the usual Ferry-Tobolsky time-temperature superposition method with consideration of the theory of rubber elasticity. The application of these methods to a relaxation process that occurs in the glassy state appears questionable. Illers (65) suggests another superposition method. The two methods give differing results for the apparent activation energies and their temperature dependence. Ishida (59) and Boyd (74) investigated 6-nylon and 6,6-nylon in a frequency range from 50 Hz to 1 MHz using dielectric methods. In this case also the relaxation time distribution shows itself to be temperature dependent, and the apparent activation energy ($A_g = 14.5$ kcal./mole) agree well with those derived from mechanical measurements (65).

The motion of short methylene chains, which becomes free at even lower temperatures (γ -process), was studied by Woodward, Crissman & Sauer (69), Kawaguchi (76), and Illers (65, 70) after Wilbourn (15) had already reported that this process always appears when three or more CH_2 -groups occur in the main (or, respectively, side) chain of a polymer. The area under the loss curve increases approximately linearly with the number of CH_2 -groups between the carboxylic amido-groups (76); nevertheless, this relationship could be studied more effectively by means of the imaginary part of the complex modulus. The addition of water and alcohols causes a sharp decrease in the intensity of this γ -process (69, 70).

A considerable increase in the elasticity or shear modulus in relation to the same quantities in dried polyamides is observed in swollen polymers below T_g (65, 69, 70). With respect to this, it is noteworthy that, according to Starkweather (82), sorption of water in polyamides increases the density of the swollen polymer so long as the temperature is below T_g . Apparently, through the addition of these liquids, the H-bridges are broken up and a more dense molecular packing is made possible, indicating an increase in the forces of molecular interaction.

According to Jacobs (73), the behavior of polyamides described here is confirmed by dynamic-mechanical experiments on similarly constituted polyurethanes.

POLYESTERS AND POLYCARBONATES

Several studies of the molecular motion in polymethyleneterephthalates have appeared recently. From dynamic-mechanical measurements on polyethyleneterephthalates and related polymers in a temperature range between 200 and 400°K., at various degrees of crystallization and draw ratios, two relaxation processes have been discovered according to Kawaguchi (83). The loss factor maximum that occurs at 200 Hz in the neighborhood of 370°K. is

apparently caused by ε rearrangement of segments of the principal chain and is identical to the glass transition. The temperature of the loss maximum increases with increasing degree of crystallization. Detailed studies by Breuer, Illers & Jenckel (84) on polyethyleneterephthalates that had been completely crystallized at various temperatures have shown that the temperature of the damping maximum goes through a maximum value at a degree of crystallization equalling 30 per cent. The influence of the crystallinity on T_g has also been studied by Uematsu & Uematsu (85). The volume of samples tempered at various temperatures and then quenched was measured and the glass temperature thus obtained was compared with a theoretical relation between T_g and the degree of crystallization. Studies of a more exact and a broader nature concerning these questions are still lacking.

A smaller maximum at about 230°K. is independent of the degree of crystallization and of extension. Its intensity is raised by the addition of water and lowered by the addition of other organic solvents. From the behavior of several similarly constructed polyesters, it is concluded that this transition is attributable to a thermal motion of atomic groups between the cyclic groups.

Comprehensive studies of the molecular motion of polymethyleneterephthalate with 2 to 10 methylene groups per monomer were carried out by Land, Richards & Ward (86), Farrow, McIntosh & Ward (87), and Ward (88) by means of dynamic-mechanical, nuclear magnetic resonance, infrared, and x-ray methods in the temperature range between 90 and 470°K. Through deuteration of the benzene ring or of the methylene groups, it was proved that above T_g both the benzene rings and the methylene groups execute considerable molecular motion inside the amorphous regions, while in the crystalline regions only the methylene groups execute hindered rotation. The low temperature loss maximum, which is displaced to lower temperatures for longer methylene chain length, as is T_g , is probably a superposition of two closely neighboring relaxation processes. The CH_2 -motion, which begins at lower temperatures, supposedly goes over to the COO -groups with rising temperature.

There is a similarity in the structure of polyethyleneterephthalate and the polycarbonates in so far as both contain a succession of aromatic rings fastened together by more or less mobile intermediate pieces. Because of this, we make reference at this time to several studies of polycarbonates. The first dielectric studies on a polycarbonate made from 4,4'-dioxydiphenyl-2,2-propane over a large temperature range (83–523°K.), at frequencies between 1 and 316 kHz, come from Müller & Huff (89) and Krum & Müller (90). For this polymer, T_g is given as 422°K. by Schnell (91). The dielectric loss maximum, which is related to T_g , occurs at 1 kHz at around 448°K. and is displaced to higher temperatures with rising frequency, in accordance with an activation energy of 115 kcal./mole. In comparison to polyethyleneterephthalate, segmental rearrangement sets in at higher temperatures, apparently because the relatively short intermediate pieces joining the phenyl groups

lend a greater stiffness to the macromolecule. The reason why this polycarbonate retains good flexibility even at quite low temperatures in spite of a high value for T_g , is because it exhibits a second definite relaxation process at low temperatures, or short experimental times. This leads to the formation of a loss maximum at about 193°K. and 1 kHz in the dielectric experiment and, as for polyethyleneterephthalate, is supposedly caused by the reorientation of the carbonyl dipoles in the electric field.

The temperature dependence of the dynamic-mechanical behavior of this polymer (I), as well as of a polycarbonate made from 1,5-naphthylene-di-(β -oxyethyl ether) (II), was investigated by Illers & Breuer (92). The temperatures of the two maxima described above are, at 1 Hz: 428 and 176°K. respectively for (I), and 373 and 183°K. for (II). From low frequency mechanical measurements, it may be clearly seen that, similar to the situation found in polyethyleneterephthalate, the low temperature maximum is due to the superposition of two closely neighboring relaxation processes whose individual natures are still unclear. The greater tendency to crystallization of the polycarbonate (II) reveals itself clearly in these measurements.

POLY- α -OLEFINS

With a testing time of 1 sec. and at about 130°K., linear polyethylene (polymethylene) exhibits a maximum in the mechanical damping that corresponds to motion of CH_2 -groups located in the amorphous regions (15, 16, 23). Since no further relaxation process occurs below the melting range of the crystalline regions, one may conclude that this maximum is correlated to the glass temperature. This is confirmed by measurements of the temperature dependence of the specific volume made by Swan (93) and by measurements of the linear thermal expansion made by Dannis (94), who find 140 and 145°K., respectively, to be the T_g for high pressure polyethylene. In branched polyethylene, which contains a more or less large number of side chains consisting mainly of ethyl and butyl groups, an additional relaxation process takes place in the amorphous regions at 1 sec. and 248°K., resulting from motion of those chain segments containing side groups (15, 16, 23). With greater concentration of side groups, the intensity of this relaxation process increases. This polymer can be considered to be a co-polymer of linear and branched chains in which each component exhibits its own relaxation process. Dynamic-mechanical studies by Nielsen (95) on ethylene-vinyl acetate co-polymers support this picture and indicate that not only branches, but all non-crystallizable groups, here the vinyl acetate groups, lead to the relaxation process at 248°K. Smith and associates (96, 97) have carried out detailed nuclear magnetic resonance measurements on polymethylene and polyethylene. The results of these authors support the conclusions drawn from mechanical and dielectrical measurements. A critical consideration of the low temperature relaxation process ($T_{\text{max}} = 130^\circ\text{K.}$) of polyethylene seems to be important. It is generally supposed that only CH_2 -chains in the amorphous regions take part in this process. The reason for

this interpretation is the proportionality between the intensity of the corresponding $\lg\delta$ -loss peak and the amorphous fraction. As mentioned before, however, neither the loss-factor $\lg\delta$ nor the logarithmic decrement should be used for quantitative discussions, but the loss modulus E'' or G'' . An examination of published results with regard to this problem shows that the intensities of the mechanical γ -peaks have constant E'' -values for all degrees of crystallinity. This means that the CH_2 -groups of the crystalline and amorphous regions take part in this relaxation process (245). As one consequence the question arises whether there is any relation between this γ -process and the glass transition of polyethylene. Cole & Holmes (246) draw the same conclusion from their x-ray measurements. The same considerations are valid for the corresponding γ -process in polytetrafluoroethylene (see below). The interpretation of the γ -processes in polyamides, polyurethanes, and other polymers should also be examined with regard to the apparent question.

A theoretical consideration of the effect of crystallinity on the viscoelastic properties of the polyethylenes is presented by Takemura (98). Since the Ferry time-temperature method could not be applied to earlier results on crystalline polymers (99), a new reduction method is suggested that takes the degree of crystallization and the draw ratio into account. This new method is successfully applied to various polyethylenes by Nagamatsu, Yoshitomi & Yokota (100) and Nagamatsu, Takemura, Yoshitomi & Takemoto (101). This method allows a determination of the degree of crystallization that gives good agreement with other methods. On the other hand, Hideshima (102) shows, using creep studies in the region of the β -dispersion, that the application of the normal reduction method is possible in the temperature range between 218 and 323°K. and that the relaxation time temperature dependence obeys the Williams-Landel-Ferry equation (18). Apparently, the normal reduction method may be applied as long as no change in the degree of crystallization or in the crystal structure occurs in the temperature range studied, a point also made by Nagamatsu & Yoshitomi (103).

The physical properties of mixtures of linear and branched polyethylenes were studied by Uematsu & Uematsu (104). They set up the relationships between the dynamic elasticity modulus and the dielectric constant on the one hand, and the density, or specific volume, on the other. Finally, Anderson, Roper & Rieke (105) compare the tensile strength of polyethylene-styrene graft polymers with that of polyethylene-polystyrene blends, and find that the graft polymers have better properties as compared to those of pure polyethylene and the blends.

Recently, various other poly- α -olefins have been investigated, since thereby the influence of controlled branch length on molecular motion can be studied. Segmental motion in poly-1-butene, according to Woodward, Sauer & Wall (106), causes a mechanical damping maximum at 300°K. and 850 Hz. Corresponding effects occur in the same region with polypropylene and

branched polyethylene. As is to be expected from the studies by Wilbourn (15), motion of the side groups leads to a relaxation process at 150°K. and 3160 Hz, which is absent in polypropylene. A regular decrease in the glass temperature from 253°K. for polypropylene to 208°K. for poly-1-octene follows from measurements of the thermal extension done by Dannis (94) on polypropylene, poly-1-butene, -pentene, -hexene, and -octene. This is the expected behavior and is already known for the poly-*n*-alkylmethacrylates; namely, the long mobile side groups decrease the packing density of the macromolecules. Because of the weakening of the forces of intermolecular interaction, the thermal energy suffices for the beginning of segmental motion at lower temperatures, if the side chain is long enough. Sauer, Woodward & Fuschillo (107) obtain an interesting result from studies of the temperature dependence of the specific volume and of the second moment of polypropylenes and poly-1-butene. Below 200°K. the specific volume of poly-1-butene is smaller than that of polypropylene, despite the crystallinity of polypropylene being about double that of poly-1-butene. Between 200 and 280°K. the increase in the specific volume of poly-1-butene is larger than that of the polypropylene. Similar behavior is found in the temperature dependence of the second moment. From earlier measurements (108, 110) it is known that the CH₃-groups in polypropylene begin a weak hindered rotation below 80°K., which becomes stronger in the neighborhood of T_g . With poly-1-butene, such behavior does not seem to be present, but rather, the number of the side groups taking part in hindered rotation increases steadily with rising temperature until T_g is reached. From these studies the great difficulty of determining the degree of crystallization by means of nuclear magnetic resonance or density measurements can be appreciated.

A comprehensive study of ten different propylenes was accomplished by Nishioka *et al.* (109). Nuclear magnetic resonance measurements were made between the temperatures of 90 and 470°K., and x-ray measurements were made at room temperature. The results given show clearly that segmental motion in the amorphous regions is more strongly hindered in the isotactic polypropylenes than in the atactic. The apparent activation energy for segmental motion was given as 13 kcal./mole in the former and as 7 kcal./mole in the latter. It should be pointed out that the apparent activation energies derived from nuclear magnetic resonance measurements are always much lower than those derived from mechanical or dielectrical relaxation measurements. The reason for this seems to be an open problem still [see also (29) and (247)].

POLYMERS CONTAINING FLUORINE

Polytetrafluoroethylene is a partially crystalline polymer whose degree of crystallization can be varied over wide limits through appropriate thermal treatment and is, therefore, very suitable for the study of the influence of crystallization on the visco-elastic behavior of molecular motion. Detailed

studies by methods of relaxation spectrometry and nuclear magnetic resonance have led in recent years to considerable clarification of the molecular processes that take place in this material. While Nagamatsu, Yoshitomi & Takemoto (111) have reported on the tensile relaxation behavior, more recent studies by Becker (112), McCrum (113), and Illers & Jenckel (114) deal with the dynamic-mechanical behavior in the temperature range from 80°K. to the melting point of the crystalline regions ($T_m = 580^\circ\text{K.}$); altogether these papers cover a range of frequency from 10^{-1} to 10^3 Hz and give consistent results. A relaxation process occurring at about 170°K. and 1 Hz with an apparent activation energy of 18 kcal./mole is—corresponding to the low temperature process in polyethylene—attributable to rearrangement processes of very small CF_2 -segments inside the amorphous regions (see above). In the temperature range between 293 and 303°K., the structure of the crystalline regions is altered, as was already found by x-ray measurements by Bunn & Howells (115). This transition still has not been found in nuclear magnetic resonance experiments. In dynamic-mechanical studies the structure change leads to maxima in the $\lg \delta$. These maxima are attributed to different rearrangement processes in the various modifications and vary from the usual maxima in that they are bound to the transition temperature T_u ; i.e., their position on the temperature scale will not vary with frequency (114).

The time-temperature superposition method can be applied only separately to temperatures $T < T_u$ or, respectively, $T > T_u$ (111). A further relaxation process in the amorphous regions leads to a maximum in the loss factor that, at 1 Hz, occurs at temperatures between 350 and 390°K., depending on the degree of crystallization. This is supposedly brought about by the release of the motion of the larger chain segments above T_g , which is also indicated by x-ray studies of Kilian & Jenckel (116). From measurements of the glass temperature of vinylidene-fluoride-perfluoropropylene copolymers, Tobolsky (117) infers that, because of the great rigidity, T_g for polytetrafluoroethylene must be above room temperature.

McCrumb (118) reports on his detailed studies of the temperature dependence of the torsion modulus and internal friction for co-polymers from tetrafluoroethylene and hexafluoropropylene at about 1 Hz and compares these results with those obtained for polyethylene and polypropylene. The behavior of the different relaxation processes under varying concentrations of the co-polymers is in agreement with results previously described.

The time-dependent elastic modulus of polytrifluorochloroethylene was determined from relaxation experiments between 279 and 353°K. by Nagamatsu & Yoshitomi (103). It is possible to give a phenomenological description of the results with the help of the relaxation spectrum under application of the time-temperature superposition method. Since the measurements do not extend into the region above T_g , the factor T/T_g (T_g = reference temperature) that comes from the theory of rubber elasticity was not taken into account. The apparent activation energy of 100 to 200 kcal./mole, how-

ever, has the usual order of magnitude for segmental rearrangement above T_g . Illers & Jenckel (119) give $T_g = 346^\circ\text{K}$. for perfectly amorphous quenched polytrifluorochloroethylene from expansion measurements; this is in agreement with the x-ray results of Kilian (116) and the nuclear magnetic resonance measurements of Nishioka (120). The loss factor maximum occurring at 1 Hz and about 373°K . is displaced sharply to lower temperatures through the swelling of the polymer in low molecular weight liquids, while a weaker relaxation process occurring at about 253°K . remains stationary. This gives further indication that the high temperature relaxation process is due to a rearrangement of the segments in the ordinary sense. This view is contrary to the discussion given by Baccaredda & Butta (121), who come out with a $T_g = 215^\circ\text{K}$. from their dynamic-mechanical measurements. Finally, the reader is referred to investigations of Krum & Müller (90), who measured the dielectric loss of polytetrafluoroethylenes and polytrifluorochloroethylenes having differing thermal and mechanical pretreatment over a wide frequency and temperature range. The relaxation processes discussed above are also detected by this method.

Over and above the significance of relaxation spectrometry as a tool for basic research, these methods hold out the possibility of predicting to a great extent the behavior of high polymers under conditions of usage and processing, and of directing the development of new polymers with predetermined properties. There is a general tendency to replace the technological testing processes to a great extent with scientific methods. The extent to which this is already possible today is convincingly demonstrated by Bohn & Oberst (122) and Staverman & Heijboer (123).

STRUCTURE AND STRUCTURAL CHANGES IN HIGH POLYMERS

Macromolecules are characterized by a common structural property. They are composed of a large number of covalently bonded chain components. As a result of varying conditions of polymerization, there are many possibilities as to how the individual chain components may be arranged in a macromolecule (similar or different chain components in linear or branched macromolecules). Because of a free rotation about the C—C bonds in the chain, the molecule also can exist in a large number of spatial configurations. These can conveniently be characterized: (a) by the shape of the chain (for example, coiled, partially extended, or folded), and (b) by the arrangement of the atomic groups in the individual polymer molecule ("intramolecular order"). Many molecular systems can crystallize, in spite of this complex structure. Nevertheless, crystallization is incomplete, and there are crystalline regions next to those that are of the same order as the melt (amorphous regions).

The extent to which crystallization equilibrium may be approached depends upon (a) the individual properties of the macromolecule and (b) the conditions of crystallization (thermal history). In general, crystallization

equilibrium cannot be attained. The kinetics of crystallization follow particular laws to a certain extent. Crystal structure is anisotropic in a characteristic manner, since the direction in the crystal lattice in which the long axis of the molecule lies is distinguished by its very nature. Further, there are typical morphological structures (spherulites) which are observed. These may form, for example, in laminar units in which the molecules lie folded. By means of selected examples, these problems will be discussed in what follows.

The melt of high polymers.—As is generally known, there is local order in liquids, which may be of a different nature from one substance to another because of the individual properties of the molecules. Exact studies of the configuration of a macromolecule in the melt are still scarce. A direct x-ray structure analysis is made difficult because inter- and intramolecular distances, which are of the same order of magnitude, determine the diffraction picture (124 to 126). According to x-ray measurements, the liquid interference ("amorphous halo") broadens in polyethylene, polyisobutylene, and atactic polypropylene, in that order (127). This effect is attributed to short branching chains that, according to their concentration, change the stereoregularity of the molecule and its mobility. Thus, there is better local order in polyisobutylene than in atactic polypropylene. A polyisobutylene molecule, with its two CH_3 -groups per monomer, is apparently more sterically regular in its structure than is the polypropylene molecule. This "steric effect" of short branching chains indicates a relatively close packing, at least to a certain extent, and a certain flexibility of the polyolefin molecules in the melt. With considerably stiffer molecules (128), as with polytetrafluoroethylene, with a co-polymer of tetrafluoroethylene and hexafluoropropylene, and with polychlorotrifluoroethylene, a dispersion in the distance statistics could hardly be detected (127). The CF_3 -group, and especially the chlorine atom, protrude to a relatively smaller extent beyond the statistical molecular cross section of the CF_2 -chain in comparison to the CH_3 -group in the polyolefins. Both 4,6-polyurethane and poly-terephthalic-acid-glycolic-ester exhibit relatively broad distance distributions. This could be ascribed to atomic groups localized in the chain that lead to specific intermolecular interactions [H-bridges in polyurethane (129) or benzene nuclei and CO-dipoles in polyterephthalic-acidglycolic-ester (130)]. A more exact analysis, carried out according to the model of Finbak (125), Bjørnhaug (126) or Zernicke & Prins (124), indicates that atactic polystyrene has extended molecular regions. The steric "blocking" ("*Sperrigkeit*") of the benzene nuclei can cause a situation in which, inside of these extended regions, the benzene nuclei on the average have the same spiral as in the isotactic crystal (132). Breaks included statistically in the chain (head-to-head or tail-to-tail polymerization) hinder the intermolecular ordering of the molecules into a crystal lattice. Miller (133) comes to a very similar opinion with samples of polypropylene quenched from the melt. Here, also, parts of the molecules are said to possess helical structure, whereby no crystal can be formed because of the "unstable smectic" arrangement of the molecules. From calorimetric

measurements on irradiated polyethylene (134, 135), it is concluded that the intermolecular order of the molecules in the melt remains to a certain extent. This memory of the melt is held responsible for the fact that in certain cases when a crystalline sample is melted for only a short time, the state of the recrystallized sample depends on its history (136, 137). Nuclear magnetic resonance measurements likewise indicate a heterogeneous structure of the melt (138). To be in agreement with this, the local order in the melt must improve in the neighborhood of the melting point of crystallizable polymers, since more and more nuclei (*Embryonen*) are formed (139, 140).

The glass transition.—From a molecular point of view, the glass transition is characterized by the fact that micro-Brownian motion is no longer possible at temperatures sufficiently below the glass temperature T_g . In a very idealized description, the equilibrium configuration of the molecules at the glass temperature is frozen in, when the melt is cooled down below T_g . In reality, rearrangements of segments of molecules are still possible to a limited extent at temperatures below T_g . This effects a gradual approach to "inner equilibrium" in time (141, 142). Because of this the position of T_g depends upon how fast the sample is cooled (or heated). Volume measurements show a discontinuous jump in the coefficient of expansion at T_g , as for example, was measured in polyethylenes recently by Gubler & Kovacs (143). Differential thermal analysis has also been introduced recently as a method of determining T_g (144).

Little is known about the structural changes that accompany the transition from the melt to the glass. X-ray measurements with strictly monochromatic radiation have shown a widening of the liquid interference, besides the jump in the coefficient of expansion (127). The relative broadening is greatest with linear polymers of sterically regular structure (for example, polytetrafluoroethylene). The segmental motion setting in above T_g broadens the spacing statistics probably because of a statistical superposition effect. This effect can be explained, at least qualitatively, by the theory of the glass transition [Hirai & Eyring (145, 146), Gibbs & DiMarzio (147)]. These authors assume that more and more "holes" occur in the polymer with increasing temperature above T_g . After-effects in the freezing region are explained by the proposition that even though a lattice contraction takes place spontaneously upon a drop in temperature the equilibrium concentration of holes is attained only slowly and, finally, not at all. Wunderlich (148) has found an increase of 2.7 ± 0.5 cal./deg. in the specific heat when the glass transition temperature is exceeded. On the basis of the Hirai and Eyring theory (see above), Wunderlich could calculate this experimental value (148).

Gibbs & DiMarzio (147, 149) consider the glass transition to be a transition of second order on the basis of the lattice model of Meyer (150), Flory (151), and Huggins (152). The important molecular quantity is the chain stiffness, which is determined by the potential barrier for rotation in the chain. Good agreement is obtained for several co-polymers between the glass transition temperature calculated from molecular structure data and the experimental values. Measurements, according to which the position of the

glass transition temperature changes with varying concentration of stereoisomers (153), indicate the sensitivity to structure of the process of freezing. A number of authors (141, 142) consciously differentiate between the process of freezing and a second order transition. According to them, internal equilibrium is not attained below T_g . The substance would not freeze if cooling were accomplished at an infinitely slow rate, but a transition would occur in this case at the thermodynamically fixed transition temperature T_u . Besides these arguments, Rehage (142) points out that the specific heat and the coefficient of expansion are greater immediately below than above T_u , whereas the opposite situation is always observed with freezing. The zero point entropy is positive for a glass. In the case of a transition, it would have to go to zero by the principle of Nernst, since internal equilibrium is assumed.

CRYSTAL STRUCTURE OF HIGH POLYMERS

A necessary but not sufficient property that a crystallizable polymer must possess is a certain steric regularity, as exemplified especially by many isotactic or syndiotactic polymers (27; 154 to 166). Linear, unbranched polymers like polyethylene or polytetrafluoroethylene (167) always exhibit a certain steric regularity, whether the atomic groups in the molecule are twisted in a periodically regular or in a statistically irregular fashion. These polymers can, therefore, form a crystal lattice without any "intramolecular" order. Such "pseudocrystals" are ordered only in the two lattice directions that are perpendicular to the long axis of the molecule (168 to 170). The situation is different with isotactic polystyrene and its variations, or with polypropylene (131, 133). Here a crystal lattice can hardly be formed if the sterically "ob-

TABLE I
SCHEME OF THE CRYSTAL STRUCTURES OF THE HIGH POLYMERS

Structure	Intermolecular Order			Intramolecular Order†
	Lateral (a)*	Lateral (b)*	Longitudinal†	
Melt	0‡	0	0	0
Pseudocrystal	1**	1	0	0
Pseudocrystal	1	1	0	1
Crystal	0	1	1	1
Crystal	1	0	1	1
Perfect crystal	1	1	1	1

* Lattice directions perpendicular to long axis of molecule.

† Lattice direction in direction of long axis of molecule.

‡ Ordering of atomic groups inside of individual polymer molecules.

§ Not present.

** Present.

structing" side groups lie twisted in a statistically disordered fashion. Therefore, the "intramolecular order" becomes important as a typical structure parameter for macromolecules. Through various arrangements of the intramolecular order, all intermediates between the pseudocrystal and the perfect crystal lattice are possible. Table I gives an overview of the high molecular crystal types as, theoretically, they could be formed. According to this, a pseudocrystal is realizable in two ways, namely that (a) the molecules themselves have no identity period or (b) the longitudinal order is not produced because of smectic displacement of the intramolecularly ordered molecules. All the structures given are characteristically anisotropic since the lattice elements in the direction of the long axis of the molecule are held together by primary valence forces.

In addition, the high molecular crystals are characteristically distorted. They have, according to Hosemann (171) and others (172, 173), a "paracrystalline" order that results from accidental statistical displacement of the lattice elements from their ideal positions. Therefore, a determination of the randomness of the high molecular lattice under consideration is a problem in structural analysis. Unfortunately, no higher order interference is usually found in the x-ray diagrams of samples that have not been specially treated. Such an occurrence could, according to Bonart (174, 175), yield a measure of the lattice perturbation. Two interferences of different order would be sufficient for this purpose. Hendus (176) has shown that the crystal lattice is opened up in one dimension with an increasing degree of branching in polyethylenes. If one assumes that the ethyl or butyl branches cannot be incorporated in the crystal lattice, this result indicates that an interaction takes place between the crystalline and the amorphous regions. Kilian & Jenckel (136) believe such an interaction is founded upon an increasing thermal expansion of the crystal lattice of polytetrafluoroethylene above T_g (373°K.). The lattice of pseudostructures is strongly perturbed in all known cases and, because of this, is expanded in comparison to the normal lattice (136, 168, 169).

A pseudostructure can arise through anisotropic thermal perturbation of the lattice as, for example, with polytetrafluoroethylene above 303°K. (115, 136). Here the two hexagonal pyramid structures disappear as shown by the diffraction diagram (136). It is assumed that because of elastic vibrations in the longitudinal direction (corkscrew-like vibrations of parts of molecules), a sort of perturbation arises as is known for liquids (115, 173). A lamellar structured crystal (see Table I) has been found at high temperatures in polyurethane (168). The polyurethane lattice is constructed from "lattice planes," in which the neighboring molecules are bonded by H-bridges (129). The weaker Van der Waal's forces act only between the lattice planes. Accordingly, if the coupling is strong in the lattice planes, the atomic groups vibrate preponderantly out of their planes on heating and so produce a measurable thermal perturbation only in the dimension perpendicular to the lattice planes. The corresponding (002)-interference in the wide angle x-ray diagram becomes less intense and more diffuse. Bonart *et al.* (173) explain

this line broadening, without giving molecular details, as a "paracrystalline" perturbation of the lattice due to thermal effects. Kilian & Jenckel (168) assume spectrally displaced scattering components, which should occur symmetrically to the original interference by extrapolation of the Born theory of lattice vibrations to larger amplitudes (177 to 179). Kitaigorodskii (180) calls the thermally produced pseudostructure the "gas crystalline state" paralleling Frenkel's "oriented melt" (181). Rotatory vibrations about the C—C bonds parallel to the chain axis supposedly occur, through which rearrangement may also take place. Such rearrangement has been detected by dynamic-mechanical measurements of the rotational transition of polytetrafluoroethylene (113, 114).

The partial crystallization of high molecular substances.—All high polymers crystallize only incompletely from the melt. This fact is confirmed by density, x-ray, and calorimetric measurements. The interpretation of the experiments has led to two views that differ in principle: (a) the two-phase model, in which crystalline and amorphous regions occur next to each other, and (b) the one-phase model, which admits of only a crystalline phase, whereby a more or less large number of discontinuities are distributed in the crystal. The discontinuities represent lattice perturbations of the second kind (171, 173). One obtains a diffuse component in the x-ray diffraction picture as a result of such perturbations. The integral intensity of these diffuse components is a measure of the number of lattice imperfections (173). In the two-phase model, the x-ray diffraction pattern can be thought of in an approximate manner as arising through the superposition of the crystalline and the amorphous spectra, whereby the total intensity is divided between the two according to the extent to which the sample is crystallized. The validity of both concepts has been demonstrated in model experiments with visible light (173).

The determination of a "degree of crystallization" (93, 153; 182 to 188) obviously has the purpose of providing a characteristic number that indicates how far the crystallization has proceeded. In the determination of the degree of crystallization from the x-ray diagram, the definite separation of the liquid spectrum is problematical since the crystal spectrum also possesses diffuse scattering components because of the paracrystalline perturbation of the lattice (171). In addition, a diffuse component occurs that comes about through thermal oscillation of the lattice elements, the magnitude and angular distribution of which, in practice, are unknown. Kilian (169) has constructed the amorphous spectrum into the total diffraction pattern according to the positions and forms of the curves. For this it is necessary that within a known angular interval only the amorphous spectrum occurs. Such is generally expected at small angles of diffraction (171). Johnson (182) has suggested a numerical-graphical method that led to contradictions at higher temperatures for poly-terephthalic-acid-glycolic-ester (169). Density measurements on variously tempered polymers could be described to a good approximation by means of the degree of crystallization determinations made by Kilian's method (136, 168, 169). Determinations of the degree of crystalliza-

tion made by different methods often result in widely differing values. The degree of crystallization resulting from density measurements depends very sensitively on the x-ray density of the crystal (169). Dole (153) discusses the calorimetric determination of the degree of crystallization. The values arrived at through these measurements are larger than the values found roentgenographically by Kilian (136, 168, 169), which values are in very good agreement with those also determined roentgenographically by Hendus (186). Both authors "monochromatized" the x-radiation after diffraction by the sample.

The single-phase model, in our opinion, represents a limiting case of the two-phase model and can have meaning only at very high degrees of crystallization. Relative large changes in density, as measured in samples crystallized in very different ways, are difficult to interpret with the single-phase model. The density change with decreasing degree of crystallization must be explained without significant alteration of the crystal density (168, 169).

Exact evaluation of the interference width of the long period interference (189) leads to a statistically loosened packing of the fold laminae for single polyethylene crystals (Marlex 50). It is to be expected that the "hollow spaces" between the laminae are not "empty" but are amorphous regions with a correspondingly low electron density. This would qualitatively explain why high pressure polyethylene exhibits a relatively broad, long-range interference attributable to the large amorphous portion. Kämpf (190) has been able to demonstrate a heterogeneous structure through electron microscope studies on crystallized polycarbonate samples. According to Kämpf (190), laminar crystal regions are attacked less than are intermediate amorphous regions in stepwise degradation of the sample. Problems of swelling show (191, 192) that the solvent—except for a few individual cases (193, 194)—penetrates only the amorphous regions. The times necessary for saturation when the swelling is begun below T_g are, for example, of the same order of magnitude for polystyrene as an amorphous polymer, as for polyvinylalcohol as a partially crystallized polymer (191, 192). In the single-phase model the diffusion of the solvent would have to take place through the "crystal." For this, one must assume a certain solubility of the swelling agent in the crystals (192) that would bring about an expansion of the crystal lattice. Gels of polyvinylalcohol however, show no change in the interplanar distances of the network in the x-ray diffraction pattern (191). Klute (195) describes the diffusion of small molecules in partially crystallized polymers on the basis of the two-phase model. The coefficient of permeability depends upon the amorphous portion and upon the "transmission function," which is supposed to recognize that the diffusion must go through a more and more complicated "labyrinth" of amorphous regions as the degree of crystallization increases. Schnell (27) has studied the diffusion of oxygen in polyethylene and has found that the time in which saturation is reached increases markedly with a growing degree of crystallization.

Superstructures in high polymers (spherulite structures).—It has long

been known that crystallizing polymers exhibit superstructures (in certain cases only after appropriate methods of crystallization) under the polarization microscope. These are generally called spherulites. The characteristic dark "maltese cross" and often also dark concentric ring systems, which may disappear at the edges, appear under the polarization microscope (196 to 205).

According to Price (206) the maltese cross of the spherulites is attributable to the zero amplitude effect of the crossed polarizers. The intermediate bright regions in the ring system are alternately positively and negatively doubly refracting. These phenomena and other optical properties of spherulites (e.g., changes that occur when the microscope table is tilted) have been interpreted on the basis of the following model. The spherulites are composed of radially directed "crystal bundles." The refractive index ellipsoids lie with their midpoints on these radii, whereby the optical axes enclose a solid angle with the radius. Progressing along a radius, the ellipsoids are rotated proportionally to the distance along the radius at a constant angle between the optical axis and the radius. It is allowed that the intermediate regions be amorphous. Keller (207) has suggested a model that, in principle, is completely equivalent to this. Keith & Padden (208, 209) also discuss how, by means of rules, one can (a) recognize an orientation of twisting, (b) determine the sense of the twisting and (c) ascertain the position of the crystallographic axis about which the twisting takes place. Schuur (210) explains spherulite formation as a kind of rhythmical crystallization. During the crystallization, the crystals supposedly "auto-orient" themselves so that the optical behavior of the spherulites can be reproduced. One of the evidences for the "auto-orientation mechanism" is that the molecules in neighboring regions are placed approximately perpendicularly to each other. The general outline of the following picture for the fine structure of the spherulites has resulted from a great number of experiments [electron and light microscopy, electron and high resolution x-ray diffraction (*Roentgenfeinbereichbeugung*), and small angle x-ray pictures]. (a) The central body of the spherulite consists of layers of laminae that arise through regular folding of the molecules. The molecules have their long axes perpendicular to the surface of the laminae. The length of the fold, therefore, corresponds to the thickness of the lamina. This is independent of the length of the macromolecule. (b) The molecules have their long axes tangential to the spherulite radii. (c) The spherulites often consist of fibrils in which the crystals are arranged in the form of a spiral. (d) The fibrils arise through twisting and splitting of the laminae. The laminae can also degenerate into stick-like fibrils through anisotropic growth rates of the crystallographic planes. The laminae, or, respectively, the fibrils, are looked upon as single crystals (211 to 216).

Laminar structures have also been demonstrated for films produced from the melt (190, 216, 217). Kämpf (190) has found pyramids of laminae even for polycarbonate films that were annealed at higher temperatures after complete suppression of crystallization through quenching. The laminar

thickness agrees with the x-ray long period (218). Electron microscope studies on films of polyurethane produced from the melt and having various thermal histories also render a relationship between the x-ray diffraction long period and the morphological structural units (219). These studies were carried out by wide- and small-angle x-ray techniques (168). From these and other studies, Fischer, Stuart & Eppe (216) have concluded that the earlier concept of a crystalline-amorphous structure of these materials is unlikely. This conclusion seems unjustifiable to us, since the existence of amorphous regions is supported especially through the electron microscope pictures of Kämpf (190), even though the selective degradation of the polycarbonate could be partially caused by a differing orientation of the crystals to the surface of the film.

Working with a much simplified model, Peterlin & Fischer (220) have been able to calculate qualitatively, from stability considerations, that a certain laminar thickness is to be expected at a given temperature. Longitudinal vibrations of a chain in the potential field of a lattice results in a minimum in the free energy density for a certain length. The parts of the chain that exceed this length become "uncoupled." The laminar thickness as a function of the temperature can be given correctly on a qualitative basis. The folding mechanism itself has not been established. The "uncoupling" of the parts of the chain that exceed the stable length can likewise lead to amorphous regions that traverse a molecule until its entrance into the next crystal. In contrast to the structure concept described above, some authors (221 to 223) support a refined concept of fringe micelles (224). Electron microscope pictures of perlon and collagen filaments, impregnated with phosphotungstic acid for contrast, show a regular structuring especially in the lengthwise direction of the fibrils. The smaller of the two periods that occur (at 100 Å) is attributed to a regular alternation between crystalline and amorphous regions since the phosphotungstic acid supposedly impregnates only the amorphous regions (221). The interpretation of these experiments leads to fibrils with a fine structure (microfibrils) in which the molecules have their long axes in the direction of the fibril and traverse alternately amorphous and crystalline regions. The roentgenographic long period is attributed to the regular alternation of crystalline and amorphous regions. Studies using small angle x-ray diffraction on polyethylene filaments given varying thermal treatments are interpreted by the authors (223) on the basis of the Hess-Kiesig model. There is no relationship between the change in the long period and the macroscopic length of the filament. No complete attempt to explain the optical behavior of spherulites with the help of the refined fringe micelle model is known to us. A start in this direction has perhaps been made by Matsuoka (139), who assumes that the spherulites form in the secondary phase of crystallization. During relaxation of the tension between the amorphous and crystalline regions, the crystals orient themselves in the prescribed manner.

Crystallization of high polymers.—The mechanism of crystallization of high polymers is more complicated than that of low molecular weight substances, because the configurational restrictions of the macromolecule give rise to special kinetic difficulties. There are basically two conceptions of the process of crystallization (139): (a) The crystals form from the melt in statistically irregular orientation, and the spherulites first arise secondarily as a result of a process of tension relaxation in the amorphous regions. (b) The spherulites form immediately upon crystallization out of the melt. The crystallization proceeds by means of secondarily induced nucleus formation on the surface of crystals already present. Price (225) has recently treated the special case of crystallization from dilute solution. The primary nucleus, whose origin is not discussed, consists of a fold lamina. This can only grow further anisotropically parallel to the fold planes. New crystal layers grow through coherent nucleus formation upon those already present. It is shown that, in the case of polyethylene under controlled supercooling, all crystals have essentially the same thickness and this thickness should increase with rising temperature. If the spherulites are assumed to grow in a disc-like formation, the calculated and measured spherulite radii are in good agreement. For the calculation one must assume different surface enthalpies for (a) the crystal boundary surfaces in which the molecule loops lie and (b) the surfaces that are perpendicular to these. A theory of the absolute growth rate of spherulites is given by Hirai (226) on the basis of the perfect crystal growth mechanism of Volmer-Frenkel and the absolute reaction rate theory of Eyring. In place of the free surface enthalpy, the "local viscosity in the neighborhood of the crystal surface" is introduced. The experimental determination of this quantity, however, is certain to be just as problematical as the determination of the free surface enthalpy. This treatment, nevertheless, does yield clear information about the flexibility of the polymer chain, as discussed by Hirai (227) in reference to polyethyleneoxide. Both theories fail to take account of the incomplete crystallization of polymers, so they represent an approximate treatment.

In contrast to these treatments, Matsuoka (139) takes nuclei formation and incomplete crystallization into account. The author extends the already existing theory of phase transitions of low molecular weight substances since he introduces into the calculation the "most probable form" of high polymeric nuclei and a limitation of the unhindered, primary crystal growth by "strained amorphous" regions. This is expected from molecular considerations, e.g., at points of branching or loops. Only the secondary crystallization leads to spherulite structures. The rate of crystallization in this case is determined by the relaxation times, during which the tension built up in the amorphous regions while primary crystallization occurred can be released. The crystals orient themselves simultaneously. Correlations must necessarily exist between the crystals so that they can orient themselves over larger regions in order that the optical behavior of the spherulites will result. This could be

attained through macromolecules built into a number of crystals. Such a molecular network is generally assumed in the case of crystalline gels (228 to 230). This network would also clearly establish the limitation of the primary crystallization. The temperature dependence of the number and size of the nuclei is also given by Matsuoka (139). X-ray measurements on the crystallization of a number of polymers given various thermal treatment, (231) resulted in essentially the same dependence. It was determined, for example, that polymers that have been quenched and subsequently annealed crystallize "stepwise" (168, 169). In the temperature range of the first step in crystallization, almost the same number and the same size of crystalline regions are formed, according to small- and wide-angle x-ray photographs. In this interpretation it is assumed that the long period is a measure of crystallite size.

According to Matsuoka (139) and others (140), more densely packed regions (embryos) occur in the melt as a result of "heterophase fluctuations." These are frozen-in through quenching and give rise to athermal nucleus formation. As long as the crystallization originates preferentially from these nuclei, the same number of crystals and the same sized crystals should be formed after sufficiently long tempering (naturally only in the statistical average).

Lauritzen & Hoffmann (140) also include molecule folding in their theory of crystallization. According to this, under the assumption of homogeneous nucleus formation, "fold nuclei" are formed only from highly diluted solutions. Lamellar single crystals grow from these nuclei. The fold length of the molecules determines the thickness of the lamina, which increases with rising temperature in agreement with experiment. This thickness of the lamina, determined by the temperature of formation in the medium, is the most important factor in determining their melting point, which lies below the melting temperature of the "infinitely extended three dimensional single crystal." For homogeneous nucleus formation only, "bundle nuclei," in which a number of neighboring molecules are included in a sort of sheaf arrangement, form out of the melt. Folded structures can arise in pure high polymers only when the bundle nuclei can grow no more, for instance, because of strain in the amorphous regions, while the crystallization proceeds mainly from heterogeneously formed fold nuclei.

In conclusion it should be mentioned that, besides the necessary regularity in the molecular structure, questions of filling space and kinetic requirements are also important in determining whether or not a macromolecular substance will crystallize (232 to 234). Braun (232) and Natta (159) have been able to show that isotactic poly-*p*-iodo- and poly-*p*-chlorostyrene do not crystallize.

The glass temperature is raised successively in the atactic *para*-substituted series fluoro-, chloro-, bromo-, and iodostyrenes. This is attributed to the steric effectiveness of the substituents (36), as is also the above mentioned effect. Mandelkern (134) concludes from the low tendency for crystallization

shown by polyisobutylene that favorable kinetic conditions must also be present for crystallization. Polymers with side groups that are sterically very obstructing can probably crystallize only if intramolecular order (usually a molecular spiral) is set up. Otherwise the molecule becomes relatively "stiff," and the mobility necessary for nuclei formation can be attained only at higher temperatures.

Melting of partially crystallized polymers.—For high polymers it can generally be considered as characteristic that they melt over a more or less broad temperature interval. With increasing temperature the extensive thermodynamic quantities such as volume, enthalpy, and entropy change continuously with increasing slope until all the crystalline portions are melted. This phenomenological behavior could be qualitatively described as a second order transition through consideration of cooperative interactions (235). Hereby, melting comes about inside of one phase that, for continuing equilibrium, converts continuously from the crystalline state of order to the melt. This opinion was put forth primarily because there was some question as to the appropriateness of handling the relatively small crystalline and amorphous regions as two thermodynamically independent phases, because evidently some of the macromolecules belong to both regions (236). The cooperative interactions are described by a parameter whose molecular interpretation is difficult. This treatment is in contrast to the two-phase model in which the amorphous and crystalline regions are taken to be established phases with consideration of the boundary surfaces. According to this, the melting of a crystal occurs at constant temperature, the melting temperature T_m . At continuing phase equilibrium the extensive quantities volume, enthalpy, and entropy change discontinuously. In this case we have the fundamental problem of explaining why high polymers, in general, melt over an interval of temperature.

According to Flory [included in a discussion by Mandelkern (134)] there are, at sufficiently macromolecular weights, three causes for the lowering of the melting point of high molecular crystals (basically the following is true also for micromolecular crystals): (a) the "surface effect" for sufficiently small crystals, (b) low molecular weight substances that are dissolved in the amorphous regions as a second component, and (c) "noncrystallizable sequences" that are built into the macromolecule and have, in addition to the direct limitation of crystal growth, an effect similar to that of a second component in the amorphous regions. For example, co-polymers with only one crystallizable component, or short-chain, branched polymers whose side groups cannot be incorporated into the crystal fall into the last group (134, 237). The lowering of melting points has been measured in a number of cases and has confirmed the theoretical expectations [summarized by Mandelkern (134)]. Two further effects are predicted by the theory, especially in the case of co-polymers or branched polymers. With increasing concentration of the noncrystallizable component, (a) the degree of crystallization decreases, and (b) the interval of melting becomes larger (237). This effect has been con-

firmed with various branched polyethylenes (95, 143, 153, 238, 239). A direct fitting of the calculated degree of crystallization to the measured values was always possible only in the neighborhood of the melting point. At temperatures below T_s the deviations can become considerable, a result that must generally be expected since in reality the crystallization equilibrium cannot be attained in this region. According to Flory (237, 240), pure homopolymers having sufficiently large molecular weight and sufficiently large crystals should melt with the sharpness characteristic of small molecules. According to Kilian (136, 239) this is, in fact, the case for polytetrafluoroethylene that was tempered for a long time just under T_s , even though the sample (92 per cent crystalline) was not completely crystallized as required by the theory. On the other hand a co-polymer of tetrafluoroethylene and hexafluoropropylene melts at a considerably lower temperature and over a broad temperature interval. The CF_3 -groups block the crystal growth in the direction of the molecular long axis, hence on the average only much smaller crystallites can form than is the case for the unbranched polytetrafluoroethylene. At the same time, in agreement with the theory, the degree of crystallization of the co-polymer is much lower than that of polytetrafluoroethylene. Peterlin (241), who has found "sharp" melting for a polyethylene single crystal (Marlex 50), but "broad" melting for an extruded film, arrives at a similar result. It can also be assumed here that the broad melting of the film is to be attributed to the crystallite size distribution at a correspondingly lower average crystallite size. Kilian *et al.* (169, 239) have studied this question using x-rays with polyurethane and poly-terphthalic-acid-glycolic-ester. In this study, melting in a temperature interval is characterized by the fact that "selectively" the smallest and most distorted crystallites melt first, as is also expected from Flory's theory (237). Selective melting must be assumed since the long period increases with the first step in melting (decrease in degree of crystallization). That the long period is a measure of crystallite size is indicated because the half-value width of the wide-angle interference decreases as the long period grows (168, 169, 239). (Very small crystals produce a line broadening in the wide-angle diffraction diagram as a function of their size.) The lower the temperature of crystallization of the polyurethane, the longer was the long period and the lower was the temperature at which the first melting occurred. Thus, the crystallite size and distribution about the average value can be altered through various thermal pretreatments. Zachmann & Stuart (185) were able to show, by means of density measurements on poly-terphthalic-acid-glycolic-ester, that partial melting occurs relatively quickly with heating. "New crystallization" directly succeeds this process. Both processes are superimposed, according to the rate of heating, to a different extent during the melting of the polymers. Partial melting with subsequent new crystallization is also assumed by Posner, Mandelkern *et al.* (223) in their study of polyethylene filaments having different thermal pretreatment (study of melting of high polymers) (134). Gubler & Kovacs (143) have calculated the crystallite size distribution of polyethylene from the

melting interval and the known melting points of short chain paraffins. For this calculation it is assumed that melting over an extended temperature range is primarily a result of the crystallite size distribution. Mandelkern (134) refers to measurements on polymer-solvent systems on cross-linked or oriented samples, all of which find a satisfying interpretation on the basis of the Flory theory.

The high melting points of polytetrafluoroethylene and polyacrylonitrile must apparently be attributed to chain stiffness (242, 243). The individual rotation isomers exhibit such a large difference in energy that the melt has a relatively small entropy as a result of this restriction of configuration. Dole & Wunderlich (153, 244) arrive at an analogous interpretation through studies of polyamides.

The theories of crystallization and of melting rest almost exclusively upon the concept of the two-phase model. The far reaching experimental confirmation of the theoretical conclusions justifies the viewpoint that the single-phase model can probably be important only in the limiting case of a very high degree of crystallization. The most fundamental difference between the crystallization and melting behavior of high polymeric substances in comparison to low molecular weight models appears to us to exist in that crystallization equilibrium in general is not attainable because of the kinetic and steric restrictions upon the configuration of a macromolecule.

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THE STATISTICAL MECHANICS OF CHEMICAL PROCESSES¹

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There has been no general article on statistical mechanics in these *Reviews* since 1958. Nevertheless, this article makes no attempt to cover the complete literature on statistical mechanics in the ensuing years. Rather I have picked selected topics that I consider important, or that interest me particularly, and have tried to cover these topics in some detail. The amount of space allotted to a given topic reflects to a large extent my own interests, with two noteworthy exceptions. First, the article of Rice & Frisch (1) in Volume 11 of these *Reviews* was devoted completely to the statistical mechanics of irreversible processes; it was decided to omit discussion of the many interesting papers on irreversible processes that have appeared in the last year in order to restore some sort of balance. Secondly, in my opinion some of the most important recent advances in statistical mechanics have arisen in connection with the application of mathematical techniques originating in the study of the quantum theory of fields to the many body problem. These techniques are most useful for the study of systems in or near their ground state and have been applied mainly to the study of superfluidity and superconductivity. Such applications are not particularly "chemical," and so it was decided to interpret the title of this article to mean that they should be omitted. However, both of these self-imposed rules have been violated in the section of this review dealing with hard sphere systems in order to make the coverage of this topic more complete. Otherwise, the words "chemical processes" have been interpreted quite elastically.

The reader will note the paucity of references to the Russian literature. This lack has arisen because the translated journals available to me were of very limited variety and contained very few articles on the subjects chosen for discussion here.

Books.—Quite a number of books on statistical mechanics have appeared since 1958. Among these are texts by Chisholm & de Borde (2), Aston & Fritz (3), and Hill (4). A much revised second edition of the well-known book by Landau & Lifshitz has been translated into English (5). The famous critical article by Ehrenfest & Ehrenfest has also been translated (6) and is just as worthwhile reading today as it was in 1912, when it was originally published.

On the more mathematical side, a translation of Khinchin's book on quantum statistics (7) has been published. This is a companion to his well-

¹ The survey of literature pertaining to this review was concluded in November 1960.

² Contribution No. 2656.

known work on the mathematical foundations of classical statistical mechanics (8). The monograph by Kac (9) on probability theory and its relations to statistical physics can be recommended as much for its delightful style as for its scientific content.

Two of the volumes of the new *Handbuch der Physik* that have appeared to date contain articles of great interest for statistical mechanics. These are: Vol. III/2, *Principles of Thermodynamics and Statistics*; and Vol. XII, *Thermodynamics of Gases*. Vol. III/2 contains the following articles: "Thermodynamics, Classical and Statistical," by E. A. Guggenheim (10), "Axiomatik der Thermodynamik," by G. Falk & H. Jung (11), "Prinzipien der Statistischen Mechanik," by A. Münster (12), "Thermodynamik der Irreversiblen Prozessen," by J. Meixner & H. G. Reik (13), "Probability and Stochastic Processes," by A. Ramakrishnan (14). The articles of theoretical interest in Vol. XII are: "Theory of Real Gases," by J. E. Mayer (15), "Principles of the Kinetic Theory of Gases," by H. Grad (16), and "Transporterscheinungen in Gasen von Mittleren Druck," by L. Waldmann (17). All of these contributions can be highly recommended.

The November 1960 issue of the *Journal of Chemical Physics* (18) is a memorial issue, dedicated to the memory of the late John G. Kirkwood, who contributed so much to statistical mechanics. This issue appeared too late for individual articles to be reviewed here; however, the majority of the articles deal with problems which are pertinent to this review, so that it seems proper to cite the entire issue for reference.

Hard spheres.—The theory of systems consisting of rigid elastic spheres has received much attention recently and it seems worthwhile to attempt a relatively complete summary. The equilibrium and transport properties of classical systems, as well as the low temperature equilibrium properties of quantal systems have been studied. Rigid spheres are of considerable interest as a model, not so much because of their similarity to actual molecules, but because the Boltzmann factor and the collision dynamics of rigid spheres are simpler than for real molecules and yet moderately realistic.

Kirkwood & Boggs (19), in 1942, studied the approximate integral equations governing the equilibrium properties of a dense system of hard spheres. The most striking result of their analysis was the prediction of a phase transition at a volume significantly greater than the close-packed volume. For many years arguments raged about whether this transition was a property of the hard sphere model or an artifact of the approximations used in the theory. It has now been quite definitely established that the phase transition is real!

Alder & Wainwright (20, 21, 22) have studied hard sphere systems of 32 and 108 particles by actually solving the equations of motion of the particles on a high speed computer. The pressure was then calculated by evaluating the collisional momentum transfer and using the virial theorem. A second method was the evaluation of the radial distribution function and use of the hard sphere equation of state, which relates the pressure linearly to the

radial distribution function at contact. More recently, Alder & Wainwright (23) have investigated the effects of the number of particles on the computed results. They find that the isotherms are insensitive to particle number if this number exceeds 108. Wood & Jacobson (24, 25) have used a computer to determine the equation of state by the Monte Carlo method. In this method, particle positions are changed by the computer in a random way and the radial distribution function is calculated. The results of the two methods are in excellent agreement. They show that at a volume about 50 per cent greater than close-packed, the system can exist at two pressures. Furthermore, in the low pressure state the particles remain in an ordered arrangement; the condensed phase is a solid. Because of the small number of particles that can be handled, statistical fluctuations in the transition region are large, and the thermodynamic details of the transition are not yet clear. The indications are that the transition is first order. A preliminary report on a Monte Carlo equation of state for mixtures of hard spheres has also appeared (26).

A review of computing machine methods in statistical mechanics has been given by Fisher (27). Wood & Jacobson (28) have also given a review with emphasis on the technical details of the computing procedure.

Reiss, Frisch & Lebowitz (29) have been able to reproduce the low density branch of the hard sphere PV curve by very ingenious analytical arguments. They note that, for rigid spheres, the only part of the radial distribution function that contributes to the equation of state is the value on contact $g(a)$, where a is the diameter of the spheres. Then $g(a)$ is shown to be related to a function $G(\lambda)$ which determines the density of spheres in contact with an impurity particle of diameter λ , $\lambda \leq a$. $G(\lambda)$ is, in turn, related to the reversible work of forming a cavity of radius at least λ in the fluid. Further properties of $G(\lambda)$, based on the geometry of hard spheres and on thermodynamics, are deduced, enabling $g(a)$ to be approximated quite well over a wide range of density. The equation of state is almost indistinguishable from that of Alder & Wainwright on the fluid branch of the isotherm. The authors also discuss the surface tension of a rigid sphere fluid (it is negative) and make some remarks about $g(r)$ for $r > a$.

Reiss, Frisch, Helfand & Lebowitz (30) have also considered the addition of a hard sphere to a real fluid, whose molecules are assumed to have hard cores in addition to any attractive potential. The chemical potential of the hard spheres can be determined by the same method as discussed above. The Henry's law constant for the hard spheres is calculated and compared with experimental values for helium and argon in benzene. For these rare gas atoms the attractive forces are sufficiently weak that the authors feel justified in neglecting them as a first approximation. The attractive forces can be taken into account in an approximate way, and values of the latent heat of vaporization calculated. This was done for several pure liquids, and the results agree surprisingly well with experiment.

Rice (31) has also discussed the system of hard spheres. He considers that there are two possible types of geometric arrangement for the system:

a random arrangement, and a regular arrangement where the geometry is similar to that in a close-packed system. By considering the entropy of these arrangements at small volumes, the virial coefficients for hard spheres, the free volume, and by some judicious interpolation, he has constructed the equation of state of the system. According to his calculations, a first order transition, if it occurs at all, should occur at a volume 80 to 90 per cent larger than close packed. Possible modifications of the equation of state, in the event that there is a gradual instead of a first order transition, are discussed briefly and qualitatively. Rice (32) has also noted that the approximation to the function $G(a)$ of Reiss, Frisch & Lebowitz (29) cannot hold at the maximum density of the random arrangement. Nevertheless, the approximation seems to hold well at only slightly lower densities.

Stillinger (33) has presented an interesting alternative approach to the equation of state for a hard sphere fluid. He shows that if one makes the superposition approximation, or if one assumes that the excess density near a pair is additively composed of single particle contributions, then the determination of the equation of state is reduced to the solution of a non-linear differential equation connecting pressure and density. The two hypotheses give rise to different equations. Solution of the equations agrees with the Monte Carlo calculations only up to $\rho a^3 = 0.4$ for the superposition approximation and $\rho a^3 = 0.2$ for the linear field hypothesis. Here ρ is the number density and a the sphere diameter.

Other attempts to find analytical methods that will approximate to the results of the machine calculations have been made by Temperley (34) and Burley (35).

A good deal of work has also been done on the transport properties of a dense hard sphere system. The well-known generalization of the Boltzmann equation to a dense hard sphere fluid by Enskog (36, 37) has been questioned by Rice, Kirkwood, Ross & Zwanzig (38, 39). The collision integral in any Boltzmann-like equation contains the factor $f_1' f_2' f_1 f_2$, where the f 's are the singlet distribution functions for molecules 1 and 2, respectively. Unprimed f 's refer to pre-collisional phases of the particles, primed f 's to post-collisional phases. In the Enskog equation, the relative position variables in the pre- and post-collisional factors are displaced by $2a$ where a is the hard sphere diameter. In the work of Rice *et al.*, the positions are the same in both terms. This leads to coefficients of the density dependent terms in the thermal conductivity that differ from those computed by solution of the Enskog equation, although the shear viscosity is the same. The deviations are of the order of 6 to 12 per cent. These quantities have been computed by Rice (40).

O'Toole & Dahler (41) have given a different derivation of the kinetic equation for hard spheres which yields the original Enskog equation, contradicting the results of Rice *et al.* and a previous publication of Dahler (42). O'Toole & Dahler claim that the origin of the discrepancy lies in the highly singular nature of the hard sphere interaction which must be introduced at the very beginning of the derivation. The derivation involves writing down

the Liouville equation for the N body distribution function, contracting this equation, and then an integration by parts plus an interchange of the order of certain differentiation and integration operations. These procedures lead to boundary terms for hard spheres that are not present for potentials that only become singular at isolated points. If one assumes such a smooth potential and only specializes to hard spheres at the end of the calculation, these terms are lost. The derivation, while long, is quite straightforward and it appears that Enskog was right after all. This is a point of methodological rather than practical interest, for it may well be that the behavior of real molecules is better approximated by the equation of Rice *et al.*³

O'Toole & Dahler hesitate to make the chaos assumption, which says that the pre-collisional momenta of a colliding pair of particles are uncorrelated for dense media. This assumption is used to convert a relation between the singlet and pair distribution functions to an equation for the singlet distribution function. Their attitude may be a bit overly pessimistic. Since, according to the machine calculations of Alder & Wainwright (21) on the velocity autocorrelation function of a hard sphere system at a density half that of close packing, a particle loses almost all correlation of its velocity within five or six collisions. If there are, on the average, more than five or six collisions separating two collisions of the same pair, or if a chain involving collisions of particles 1 and 2, 2 and 3, or 3 and 1 is more than a very few collisions long, pre-collisional molecular chaos ought to be a reasonably good approximation. It is likely that these conditions are fulfilled on the gas-like branch of the equation of state.

Harris & Rice (43, 44, 45) have extended the theory of Rice *et al.* (38) to binary mixtures. In particular they have computed the mutual diffusion coefficient in a mixture with unequal masses and radii, and also the relaxation time for the approach to a Maxwellian distribution in momentum space. An interesting result is that the relaxation time is very short, just a few collision times. This agrees with the previously cited molecular dynamics calculations. Longuet-Higgins, Pople & Valleau (46, 47) have also studied mixtures of hard spheres. They avoid an investigation of nonequilibrium distribution functions by postulating *a priori* a locally Maxwellian distribution. This results in a tremendous simplification in the calculations, but also as a consequence the thermal conductivity vanishes as the density decreases instead of approaching the proper dilute gas limit. Valleau (48) has applied the same approximation to a dense system of rough spheres (relative velocity reversed on collision). One hardly knows how far to trust the results of these calculations since they are based on an *ansatz* of indeterminant reliability.

³ After this review was sent to the publisher, Professor Rice informed me (private communication) that he found that the discrepancy between the equation of Rice *et al.* (38, 39) and that of O'Toole & Dahler (41) is solely due to an error in the former. The error arises from the improper interchange of two limiting operations. Rice states that, when the interchange is carried out properly, an extra term arises. In the hard sphere limit this term is just the surface integral of O'Toole & Dahler.

Widom (49) has computed the rotational relaxation time for a rough sphere in a medium of point particles. The analysis is based on an equation of master type rather than Boltzmann type. The main result is that the effective number of collisions for rotational relaxation is $3(1+b)^2/8b$ where $b = I/ma^2$; I is the molecular moment of inertia, m the molecular mass, and a the molecular radius.

Snider & Curtiss (50) have evaluated the transport coefficients in a dense fluid of hard spheres using a modified Boltzmann equation originally derived independently by Bogoliubov (51) and Green (52). This equation differs from those previously discussed because the collisional term involves momentum derivatives of the distribution function.

Choh (53) has presented a theory of transport phenomena in dense gases along the lines suggested by Bogoliubov (54). When applied to hard spheres the theory yields just the results of Enskog for the transport coefficients when only binary collisions are taken into account. In Choh's theory there is also a contribution from ternary collisions that was not evaluated. Choh remarks that "it is quite unlikely that this contribution vanishes for rigid spheres." Hollinger (55) has derived equivalent results on the basis of a generalized chaos approximation, namely that the n particle distribution function factors into n single particle functions in those parts of phase space that may be characterized as "pre-collisional."

Molecular dynamics calculations on the nonequilibrium properties of hard sphere fluids have been carried out on a high speed computer by Alder & Wainwright (56). We regard these calculations as extremely important; they give "experimental" values of quantities such as molecular autocorrelation functions and the Boltzmann H function, which are not otherwise accessible.

The properties of hard sphere systems have been used by Smith & Alder (57) as zero order approximations in a perturbation calculation. Only the first order term in the general scheme that was developed to arbitrary order by Zwanzig (58) was used. The results, however, are in quite good agreement with the experimental equation of state of fluids at moderately high temperatures over a very wide range of densities.

The preceding discussion has been restricted to classical hard sphere systems. A considerable amount of progress has also been made in understanding the properties of a dilute hard sphere system obeying quantal laws. This understanding is primarily due to a series of papers by Yang & Lee. Their early papers on Bose-Einstein hard sphere systems have been discussed in earlier *Reviews*. The results of the early papers have now been generalized (59) to the consideration of states that arise from an unperturbed state in which the single particle ground state is occupied by a finite fraction of the particles in the system. Such states are phonon-like in nature for small wave-number, but are more like individual particle excitations when the single particle ground state is almost depleted, or when the wave-number is large. The method provides a link between the concept of phonon excitations

and the concept of condensation into the ground state. The canonical partition function is evaluated by the method of steepest descents and the thermodynamic functions for the gas phase and the degenerate phase are evaluated explicitly. A Bose-Einstein condensation is shown to arise, although the isotherms look more like those for an imperfect gas than for an ideal Bose gas.

A general method of attacking the evaluation of the grand partition function for a general many-body system has also been presented by Lee & Yang (60) and applied to the virial expansion for a hard sphere gas (61). The technique is to divide the quantum mechanical problem into two parts. The first part is the expression of the solution of the true problem (B.E. or F.D. statistics) in terms of the solution of a corresponding problem involving only Boltzmann statistics. The second part involves the treatment of diffraction effects, which still remain in Boltzmann statistics, by the introduction of a two-body operator called the "binary collision kernel." The grand partition function for a hard sphere gas is evaluated to order $(a/\lambda)^2$, where a is the diameter of the spheres and λ is the mean thermal de Broglie wave length. The binary collision expansion method holds great promise for quantum statistical mechanics. For example, it has already made possible for the first time a calculation of the quantum mechanical third virial coefficient (62). Further papers by Lee & Yang study the following problems by similar methods: the zero temperature limit for dilute hard spheres (63), the formulation of the theory in terms of the average occupation number in momentum space (64), and the degenerate phase in a Bose-Einstein condensation (65). A review of the methods of Yang & Lee has been given by Huang (66).

Garcia-Colin & Peretti (67) have computed the pair correlation function for a hard sphere boson gas as a power series in the fugacity, z , each term being calculated to order a/λ . The method used was the binary collision expansion of Lee & Yang, and the series only converge for $|z| < 1$. Garcia-Colin (68) has also used the pseudo-potential method to calculate the pair correlation function to the same order in a/λ . The two results are quite different, especially at small distances. In particular, neither calculation shows the oscillations of the distribution function that are characteristic both of experiment and of classical computations.

Ensembles.—The statistical ensembles commonly used to represent systems in equilibrium are the microcanonical (constant E, V, N), the canonical (constant V, N, T), and the grand canonical (constant V, T, μ). All of these have the common feature that the volume of the system is one of the parameters used to describe the thermodynamic state of the system. However, in practical thermodynamics, pressure rather than volume is the common independent variable. Consequently, much thought has been given to the construction of statistical ensembles in which pressure is taken as an independent variable *ab initio*.

The first such construction is due to Guggenheim (69), who described

partition functions for ensembles at constant T, P, N and constant T, P, μ . The partition function for the latter of these diverges, as was first pointed out by Prigogine (70). This comes about because P, T , and μ are not independent variables, being related by the Gibbs-Duhem equation. Brown has reconsidered the problem of the T, P, N ensemble (71). He has constructed an ensemble all of whose members have the same value of P ; the volume of the system in its n th energy level, E_n , being given by the solution to the equation $P = -\partial E_n / \partial V$. The corresponding classical theory is also given. In addition, a second ensemble is constructed whose systems consist of the molecules of interest, contained by a movable wall (considered to be part of the system!), subject to a constant external pressure P . The logarithm of the partition function, the Gibbs function divided by kT , contains the mass of the piston but in a numerically insignificant manner.

The first of Brown's ensembles, which contains no arbitrary elements, looks very attractive but Münster has shown that it is thermodynamically untenable (72). While it does give correct thermodynamic functions, it gives incorrect fluctuation formulae. The reason is that one of the independent variables, the volume V_n , is not independent of the distribution parameter P . This leads the ensemble to violate the condition that the mean-square fluctuation of an extensive variable should depend only on thermodynamic properties of the system. This condition does not apply to intensive variables, as is shown by the well-known example of pressure fluctuations in a canonical ensemble.

Sack (73) has discussed the Brown ensemble from the point of view of the general theory of transformation of variables, and has also thrown some interesting light on the divergence of the partition function for the T, P, μ ensemble. This partition function exists in general for arbitrary values of T, P, μ , but has a singularity when T, P, μ have the special values corresponding to thermodynamic equilibrium. The thermodynamically interesting quantity is not the logarithm of the partition function, as is usual, but the reciprocal of the partition function. Correct thermodynamic results may be obtained by taking appropriate derivatives of this reciprocal before passing to physically meaningful values of T, P, μ . Hill (74) has also defined some generalized partition functions that appear to fit well into the general scheme of Sack.

Dense fluids.—The theory of the radial distribution function in fluid systems has, in general, been based on one of two approaches. On the one hand, in the gas phase, it is possible to derive a power series expansion for the distribution function, the expansion parameter being the number density of the gas. On the other hand, there exist several approximate integral equations for the radial distribution function; some of these have been solved numerically. The first method is rigorous under the assumption of classical mechanics and spherically symmetrical, pairwise additive potentials of intermolecular force; but is not very useful for computation because high-order terms are exceedingly laborious to evaluate and convergence is quite slow at high density.

Recently, however, significant progress has been made in this field. Independently, and more or less simultaneously, van Leeuwen, Groeneveld & de Boer (75), Rushbrooke (76), Meeron (77 to 83), Morita (84 to 89), and Green (90) have succeeded in performing partial summations on the infinite series for the pair-correlation function. [See also Hiroike (91, 92).] This enables one to write down an exact integral equation for the pair-correlation function. At the time of this writing, no solutions of the new integral equation have appeared in the literature; however, de Boer (93) has given an oral presentation of some numerical results obtained in Amsterdam that agree quite remarkably with experiment.

The new integral equation seems to be of sufficient importance to warrant further exposition in this review. We shall follow the presentation of van Leeuwen *et al.* (75) even though the terms that are summed to yield the equation have been studied in greatest detail by Meeron, Morita, and Salpeter (94). Some background in the cluster theory of imperfect gases will be assumed.

Some twenty years ago, Mayer & Montroll (95) and de Boer (96) independently showed that the pair-correlation function in a gas could be written

$$\begin{aligned} g(r_{12}) &= e^{-\phi(r_{12})/kT} [1 + C(r)] \\ C(r) &= \sum_k \rho^k \gamma_k \end{aligned} \quad 1.$$

$\phi(r)$ is the intermolecular pair potential, ρ is the number density, and γ_k is a sum of integrals that can be described most compactly as follows: Draw the Mayer irreducible cluster diagrams (97) for $k+2$ particles; strike out the line directly joining particles 1 and 2 in each diagram; the sum of the integrals corresponding to the resulting diagrams gives γ_k .

Now Salpeter (94) has shown by regrouping terms in the expansion that

$$\begin{aligned} 1 + C(r) &= \exp [S(r)] \\ S(r) &= \sum \rho^k \gamma_k' \end{aligned} \quad 2.$$

The diagrams that contribute to γ_k' are a subclass of those that contribute to γ_k and are called "simple" diagrams by van Leeuwen *et al.* They are specified by restricting particles 1 and 2 to have no parallel connections, in the sense of electrical circuit theory.

From the set of simple diagrams it is convenient to extract a further subclass, the nodal diagrams. These are diagrams containing at least one point through which every path connecting 1 and 2' must go. All other simple diagrams are called elementary. If $N(r)$ is the contribution of the nodal diagrams and $E(r)$ that of the elementary diagrams, then clearly

$$S(r) = N(r) + E(r) \quad 3.$$

so that one can now write

$$G(r) = g(r) - 1 = \exp [(-\phi + N + E)/kT] - 1 \quad 4.$$

Now consider the set of diagrams corresponding to $C(r)$ plus the $C(r)$

diagrams to which a direct 1-2 line has been added (however, points 1 and 2 are still fixed points not to be integrated over). Let $X(r)$ be the contribution of all of these diagrams to $G(r)$, less the contribution of the nodal diagrams

$$G(r) = N(r) + X(r) \quad 5.$$

It is then possible to find an integral relation between N and X , or between G and X . This is

$$N(r_{12}) = \rho \int X(r_{13})[N(r_{23}) + X(r_{23})]dr_3 \quad 6.$$

$$G(r_{12}) = X(r_{12}) + \rho \int X(r_{13})G(r_{23})dr_3$$

This last equation is just the Ornstein-Zernike integral equation (97), where $X(r)$ is the indirect correlation function. These integral equations are of convolution type and may be solved by the use of Fourier transforms.

It is clear that if one sets $E(r)=0$, i.e. neglects all elementary diagrams, Equations 4 and 6 form a set of two equations in the two unknown functions N and X , which can be solved by iteration, as de Boer has done (93). Van Leeuwen *et al.* also indicate how it might be possible to relax the restrictive approximation $E(r)=0$ and still solve the equations, but no actual calculation has been reported.

Green has used these equations to discuss the nature of the molecular distribution near the critical point (90). His main conclusion is that the assumptions of Ornstein & Zernike (98) about the short-range nature of the direct correlation function $X(r)$ are not tenable; thus some modification may be necessary in the theory of the critical point. No further details are available at the time of writing.

The new equations, discussed above, seem to be a most important contribution to the molecular theory of fluids. However, they are derived on the basis of a selective resummation of terms in a power series expansion whose radius of convergence certainly does not extend past phase transitions. Although the resulting equations may be valid outside of the radius of convergence, in the sense that functions that enter are the analytical continuation of the functions defined by power series in the gas phase, it would be extremely desirable to have an explicit demonstration of this fact [cf. Morita & Hiroike (87)].

Molecular distribution functions of differing orders are related by a well-known set of coupled integro-differential equations. Zumino (99) has given an interesting formal solution to this set of equations in terms of functional derivatives of a generating functional. He indicates how the density expansions discussed above can be retrieved from the formal solution; however, there is no indication of a method for extracting the distribution functions from their generating functional that would be at all useful for dense fluids. Green (100) has presented a new derivation of the density expansion based on topological methods.

Before the introduction of the new integral equation, discussions of molecular distribution functions were based on the Kirkwood integral equation (101) or the Born-Green integral equation (102). Numerical solutions of these equations for hard spheres and for a Lennard-Jones potential with hard sphere cutoff were carried out by Kirkwood and collaborators (103, 104), and the results are by now well known. However, the way in which the hard core of the modified L-J potential modifies the solution for the full L-J potential had not previously been elucidated, and the solution for the full L-J potential is of considerable interest. Broyles (105) has now solved the Born-Green equation for the full Lennard-Jones 6-12 potential. The calculation was only done for one temperature $T^* = 2.74$, about twice the critical temperature, and for reduced volumes of 1.0, 1.2, and 2.5. The results are compared to the Monte Carlo calculations of Wood & Parker (106), but not with the calculations of Kirkwood and collaborators for the modified L-J potential. The agreement with the Monte Carlo calculation is, in general, fairly good beyond the first peak of the radial distribution function, but it should be noted that this is brought about by the use of an empirical scaling parameter. The first peak of the radial distribution function is "pulled in" towards the origin, relative to the Monte Carlo results and, at the higher densities, is appreciably lower than the Monte Carlo results. The first peak for the modified potential is "pushed out" from the origin relative to the Monte Carlo, as shown by Wood & Parker. Thus there is an appreciable difference between the modified and unmodified L-J potential radial distribution functions in the region that gives the most important contributions to the thermodynamic functions. It would be of extremely great interest to extend the calculations to other temperatures and also to calculate thermodynamic functions.

The Lennard-Jones potential function is the only realistic function that has been used to any significant extent in the statistical mechanics of dense fluids. Two questions now arise. How accurately does a Lennard-Jones potential represent the pair potential between atoms, and how accurately can the total potential of intermolecular force be represented as a sum of pair potentials? As far as the present author knows, the second is still an open question; a partial answer has been given to the first by Brown & Rowlinson (107). These authors have investigated the quantity

$$\Delta = [(\overline{\delta U})^2(\overline{\delta V})^2 - \overline{(\delta U \delta V)^2}]/(kT)^2$$

where U is the total potential energy of an N body system, V is the virial of intermolecular force, and $\delta U = U - \bar{U}$, etc. The superior bars indicate canonical averages. By Schwartz's inequality $\Delta \geq 0$. Brown & Rowlinson have shown that, for a Lennard-Jones 6- n potential, Δ is expressible in terms of measurable thermodynamic properties of the system and of the repulsive exponent n ; this is not true for an arbitrary pair potential. One can then use measured values of the thermodynamic functions to determine values of n compatible with the condition $\Delta \geq 0$. Using experimental data for liquid argon, Brown & Rowlinson find that $n = 12$, the most commonly used value,

leads to negative values of Δ for certain pressure and temperature ranges; $\pi > 13.3$ leads to positive values of Δ over the entire range of conditions for which data are available. Although Kihara (108) has shown that the 6-12 potential is not entirely adequate for describing even the low density properties of the rare gases, an answer is still lacking to the question of how much of the discrepancy between theory and experiment for dense fluids can be laid to approximations in the theory, how much to inadequacies in the potential function, and how much to experimental error.

Keller & Zumino (109) and Frisch & Helfand (110) have investigated the question of how much information on the intermolecular pair potential can be obtained from a knowledge of the second virial coefficient. Their conclusion is that, for monotonic potentials, a knowledge of the second virial coefficient over the entire temperature range uniquely determines the potential. For non-monotonic potentials, of the type that actually exist between atoms, the potential is not uniquely determined by the second virial coefficient, though it is partially determined. Although these investigations are quite interesting theoretically, their practical importance for determining potentials has yet to be demonstrated.

The extension of the method of molecular distribution functions to systems in external force fields has been undertaken by Steele & Ross (111). These authors write down integral equations for distribution functions under such conditions. They then discuss a perturbation technique, based on the work of Zwanzig (58), for determining the free energy of the fluid in the field, and use the integral equation to determine approximately the single particle distribution function. The technique is applied to physical adsorption problems. A derivation of the Langmuir isotherm is given, and the theory of thick films close to the condensation point of the bulk adsorbate is discussed. The methods of this paper are, in many respects, similar to the methods used to study the dielectric properties of fluids. This latter case is also a situation in which a system is in an external potential field. However, the systems that Steele & Ross study are simpler because the external field is assumed not to modify the two-body forces that act between molecules.

Time dependent distribution function.—The pair distribution function $g(r)$ has the physical significance of being proportional to the probability that a particle will be present at a distance r from a given particle, averaged over the positions of the remaining $N-2$ particles in the system. A generalization of this function has been introduced by van Hove (112) and Glauber (113) (for solids). The generalized pair distribution function $G(r,t)$ is the probability in an equilibrium ensemble that a particle is present at r at time t if a particle were present at the origin at time zero. Clearly $G(r,t)$ contains information about the average dynamical behavior of molecules, while $g(r)$ reflects their average static behavior. To date, the study of $G(r,t)$ has emphasized mainly its connection with the diffraction of neutrons by many-body systems, in which connection it was first introduced. It has a more general importance, however; in fact it may be regarded as a special case of the time-

dependent Green's functions recently introduced by Martin & Schwinger for the study of many-body systems (114).

The function $G(\mathbf{r}, t)$ is complex in general, but it has a hermitian symmetry $G^*(\mathbf{r}, t) = G(-\mathbf{r}, -t)$. The real part of $G(\mathbf{r}, t)$ has additional significance as the correlation function of the density at the origin at time zero and the density at \mathbf{r} at time t . The imaginary part (divided by \hbar) has been shown by van Hove (115) to describe the local disturbance in a medium being traversed by a neutron. Though G becomes real in the classical limit ($\hbar \rightarrow 0$), this interpretation remains valid. Fano (116) had previously noted an analogous behavior of the time-dependent distribution function for electrons in matter. There the imaginary part is related to the frequency-dependent dielectric constant.

In the classical limit $G(\mathbf{r}, t)$ may be written

$$G(\mathbf{r}, t) = G_s(\mathbf{r}, t) + G_d(\mathbf{r}, t)$$

where $G_s(\mathbf{r}, t)$ is the probability that the particle at the origin is at \mathbf{r} at time t , while $G_d(\mathbf{r}, t)$ is the probability that a different particle is at the space-time point (\mathbf{r}, t) . These functions have the limiting values

$$\begin{aligned} G_s(\mathbf{r}, 0) &= \delta(\mathbf{r}) \\ G_d(\mathbf{r}, 0) &= \rho g(\mathbf{r}) \end{aligned}$$

Note that $g(\mathbf{r})$ in van Hove's paper (112) is $\rho g(\mathbf{r})$ in our notation; ρ is the number density. Vineyard (117) has introduced an approximation that enables one to compute G_d from G_s ; namely,

$$G_d \simeq \rho \int g(\mathbf{r}') G_s(\mathbf{r} - \mathbf{r}', t) d\mathbf{r}'$$

That is, G_d is the probability that a particle at \mathbf{r}' has diffused to \mathbf{r} in time t times the probability that there was a particle at \mathbf{r}' if there was one at the origin. As Vineyard recognized, this is not entirely correct since the "self-diffusion" function, G_s , does not take into account the fact that a particle is known to have been at the origin at zero time. Vineyard has calculated G_s for several cases, the ideal gas, harmonic oscillator, and Brownian motion models, but much remains to be done here. Schofield (118) has suggested a modification of Vineyard's approximation.

Some interesting properties of $G(\mathbf{r}, t)$ for the classical case have been derived by de Gennes (119). He has calculated the second and fourth frequency moments of the fourier transforms of both G_d and G_s . The fourier transforms are four dimensional and the moments are taken with respect to the variable conjugate to t for a fixed value of the variable conjugate to \mathbf{r} . In the classical limit all odd frequency moments vanish. The remarkable fact is that the calculated moments are expressible in terms of the static pair distribution function, $g(\mathbf{r})$, and the intermolecular potential, $V(\mathbf{r})$. Another remarkable fact is that the expression for the fourth moment of the fourier transform of G_s contains a term that is identical to an expression given by Kirkwood, Buff & Green (120) for the friction constant in Kirkwood's theory

of transport processes in liquids. This clearly is no accident since G_s refers to a self-diffusion process. However, the detailed connection with transport theory remains to be worked out.

Vineyard (121) has developed a law of corresponding states for $G(r,t)$, using concepts very similar to those used by Helfand & Rice (122) in deriving a law of corresponding states for transport properties. He has also derived a sequence of integro-differential equations that link time-displaced correlation functions in much the same way as the static distribution functions are related by the familiar hierarchy of equations (123). No solutions of these equations have been presented to date. $G(r,t)$ can be expanded in a power series in the density for gaseous systems in much the same way as can $g(r)$. This is implicit in the work of Mazo & Zemach (124) who, however, expanded the space fourier transform of $G(r,t)$ rather than G itself.

From the foregoing summary, it can be seen that very little is really known concerning the details of the $G(r,t)$ function. Its study is much more difficult than the study of the static analog $g(r)$. Nevertheless, this function deserves much further investigation for it seems to be a natural tool for studying statistical aspects of molecular motions in condensed phases, and because some current theories of transport phenomena employ time-correlation functions in equilibrium ensembles. A discussion of these theories was given by Rice & Frisch in Volume 11 of these *Reviews* (1).

Free volume theory.—The cell model of the liquid state has also received its share of attention. Cohen (125) has reviewed and compared the cell theory and cell-cluster theory. In addition he has shown how techniques used in order-disorder problems can be applied to give corrections to the single-particle Lennard-Jones Devonshire theory. Different positions of molecules in a cell are considered as different components of an order-disorder system. One then has an order-disorder problem for infinitely many components. If one solves the appropriate order-disorder problem using the Bragg-Williams approximation, one is led to the Lennard-Jones Devonshire theory. Consideration of more complicated approximations, e.g., the quasi-chemical approximation, enables one to take into account, at least partially, the correlation of molecules in neighboring cells. No numerical work for comparison with experiment is reported. Dahler & Cohen (126) have formulated a cell cluster theory for binary mixtures, and then specialized to the case where one of the components of the binary mixture is holes. The cell-cluster theory without holes leads to a considerable improvement in the calculated entropy over the single-cell theory. The hope is that introduction of holes will lead to a similar improvement in the calculated liquid volume, and to an even better improvement in the entropy. This latter hope is indeed vindicated for an ideal gas in one dimension, but no calculations are reported for more realistic systems.

Levelt & Hurst (127) have calculated the thermodynamic functions for H_2 and D_2 at volumes slightly higher than solid volumes and at temperatures between about 15°K. and 150°K. from a quantum mechanical cell model.

Accepting the physical picture of the Lennard-Jones-Devonshire theory, they have computed numerically the energy levels and wave functions for an H_2 or D_2 molecule in a cell. The volume dependence of the energy levels, which is needed to find the pressure, was computed by perturbation theory, and the thermodynamic functions were then computed numerically. The authors state that experimental data do not now exist with which the theory can be compared, but an extensive tabulation of calculated thermodynamic functions is presented against the day when such comparison can be made.

Extensive calculations on the classical free-volume theory have been carried out by Dahler & Hirschfelder (128). An important conclusion of these authors is: "The agreement (with experiment) is very poor, suggesting that there is something intrinsically wrong with the free-volume concept of a liquid. . . . Thus, it appears that correlations between the motions of neighboring molecules play an important role in the structure of a liquid." This conclusion is based on the solution of Kirkwood's free volume integral equation (129) by iteration. The Kirkwood theory differs from the Lennard-Jones-Devonshire theory in permitting all molecules to wander in their cells, while the L-J-D theory puts all molecules but one on lattice points. Thus the Kirkwood theory is internally consistent, whereas the L-J-D theory is not. But Hirschfelder & Dahler find that the numerical results of the L-J-D theory for the equation of state are better than the results from the Kirkwood equation. They also find, by comparison with the results of Monte Carlo calculations (106), that both the L-J-D theory and their own results correspond to the equation of state of a metastable solid rather than a true liquid. This is probably inherent in the cell model. Modifying the theory to allow for the presence of holes does not change any results markedly for the entropy gain is offset by a large energy of hole formation. This paper by Dahler & Hirschfelder can also be strongly recommended for the excellent discussion of the physical basis of the approximations inherent in the cell model.

Alder has computed thermodynamic functions from free-volume theory for molecules interacting with square-well potentials (130). These calculations are primarily of interest in connection with a systematic study of this potential function, which is next in order of analytical simplicity to the hard sphere potential; Alder reports that he is carrying out such a study.

Other work on cell theories has been reported by Richardson & Brinkley (131), and Squire & Salzburg (132).

Eyring, Ree, and collaborators have introduced a semi-empirical partition function for the liquid state, which is arrived at by the "method of significant structures" (133 to 137). The concept of "significant structure" amounts to picking out *a priori* what one considers to be the region of phase space that gives the major contribution to the partition function and neglecting the rest of phase space. The "significant structures" that Eyring *et al.* choose for the liquid state are three in number: (a) solid-like degrees of freedom; (b) degrees of freedom associated with the degeneracy of sites in the solid-like structure, with an associated "strain energy"; and (c) gas-like de-

degrees of freedom for molecules moving in the voids between solid-like regions. A theory of liquids based on concepts of strains and dislocations has also been presented by Mizushima (138).

Assuming that the binding energy of the liquid is attributable solely to solid-like degrees of freedom, the fraction of solid-like degrees of freedom is estimated to be V_s/V where V_s is the volume of the solid at its melting point and V is the liquid volume. The partition function can then be written down from known results for solids and gases. The only delicate point is the estimation of the strain energy, which is taken inversely proportional to the available gas-like volume $(V - V_s)/V_s$, with a coefficient that is determined empirically.

A quite considerable amount of calculation has been done on the significant structures partition function. Noble gases, polyatomic molecules, fused salts, and molten metals have all been treated, and all cases yield quite good agreement with experiment except near the critical point. The viscosity and self-diffusion coefficients for liquid metals have also been investigated by dividing the viscosity into a solid-like and gas-like part and applying the Eyring theory of rate processes to the solid-like part. The agreement with experiment is quite surprisingly good. On the other hand, except for liquid chlorine (134), the calculations have all dealt with specific states of the liquid (boiling point, freezing point, etc.). No pressure-volume isotherms have been presented, and so the theory has not been subjected to the type of comparison with experiment that has become canonical for other theories of the liquid state.

While the theory of significant structures contains several empirical elements and cannot be said to have been directly derived from the exact partition function for the liquid state by any well-defined approximations, it has a certain amount of intuitive appeal. From a practical point of view, despite the theoretical lacunae in writing down the partition function, it seems to be a very attractive method of estimating thermodynamic properties of liquids. The obvious next step is to see if one can in any way extend the theory to mixtures.

Chemical equilibria.—There has been a renewal of scientific interest in the calculation of the high temperature thermodynamic properties of gases, which has undoubtedly been influenced by the technological need for such information. The usual method for computing the thermodynamic properties of gases is to calculate the internal partition function of each species present, form the equilibrium constant, find the composition, and add the partial molecular property for the several species, weighted by their mole fraction in the equilibrium mixture. This procedure may be unsatisfactory in the high temperature region for two reasons.

First, at high temperatures ionization may occur, and highly excited vibration-rotation states may give quite appreciable contributions to the partition functions of molecules. The energies of such excited states require

appreciable corrections for anharmonicity and rotation-vibration interaction; but the expressions for these corrections as given by standard perturbation theory insure that the partition function diverges. This catastrophe is usually avoided by special devices that are quite satisfactory at moderate temperatures, but whose accuracy is uncertain at high temperatures. Baumann (139) has discussed this difficulty in some detail, and has developed methods for determining how the sum over states should properly be terminated.

Second, one should realize that the method of molecular partition functions is only one approach to the thermodynamic properties of a gas. The reason is that computing the partition functions of certain molecular species involves restricting the system to occupy only a portion of its phase space, i.e. application of the idea of "significant structures." For example, the partition function of a diatomic molecule is not the same as the partition function for a two atom system. The molecule partition function only involves the bound states of the pair; the scattering, or dissociated states, are not taken into account. This suggests another method of approach that should be valid at high temperatures. That is to calculate the total partition function of the gas, treating molecule formation as giving rise to gas imperfections. This method should be especially useful at temperatures corresponding to a very high degree of dissociation. Such temperatures need not be excessively high. For example, Sinanoğlu & Pitzer (140) point out that the dissociation energy of Na_2 corresponds to $k \times 8600^\circ\text{K.}$, while at 1600°K. and 1 atm., the gas is almost all atoms.

An outline of how the method of gas imperfections could be carried out has already been given in these *Reviews* by Beckett, Green & Woolley (141), and Woolley has since given a detailed description of the general theory (142). Sinanoğlu & Pitzer (140) have developed the method further for diatomic molecules, using a Rydberg potential function to represent the binary interactions, and including valence forces. Tables that facilitate the calculation of the second virial coefficient and its temperature derivatives are given, and Na_2 is treated in detail as an example.

A drawback of the gas imperfection method is that there is no unambiguous way to compute the degree of dissociation. This is reasonable, since one gives up the concept of molecule as an independent entity in the gas. This difficulty may perhaps be resolved by the application of the methods of Stogryn & Hirschfelder (143). However, these authors give the results of calculations for the "dimerization" of chemically inert gases only. The technique is to divide the second virial coefficient into three parts, attributable respectively to bound molecules, metastable dimers, and free pairs. The metastable dimers are those pairs trapped by the centrifugal hump in the effective two-body potential. Such dimers actually have a finite mean life, according to quantum mechanics; but Stogryn & Hirschfelder show that the lifetime is generally long enough so that chemically speaking they should be considered as diatomic molecules. Bunker & Davidson (144) and Britton

(145) have also given formulations of the equilibrium constant for bound molecules and metastable dimers. These formulations refer to rather weakly bound species, though possibly this restriction can be removed.

The partition functions for a number of diatomic molecules have been calculated for temperatures from 1,000–10,000°K. by Burhorn & Wienecke (146). The standard method of summing over quantum states was used, including corrections for anharmonicity, rotation-vibration interaction, and excited electronic states. Only the partition functions are given numerically. Graphical means must be used by the reader for the thermodynamic functions. These authors have also computed the composition, density, and enthalpy of an oxygen plasma for pressure up to 30 atm. and temperatures to 30,000°K. (147). In these calculations the local electric field in the plasma was only considered insofar as it modified the ionization energy of oxygen.

For molecules of any degree of complexity, the molecular partition function may be quite difficult to compute; this occurs, essentially, because the partition function is usually calculated in terms of the normal mode frequencies and moments of inertia of the molecule and because these quantities are characteristic of the molecule as a whole. Herschbach, Johnston & Rapp (148) have shown how the calculation may be simplified, in a certain sense. As was pointed out years ago by Mayer & Mayer (97), the partition function of a molecule can be regarded as a product of volume elements, one for each atom. The volume elements express the geometrical and dynamical constraints imposed on the motion of a given atom by the presence of its neighbors. Herschbach *et al.* give explicit instructions for finding these volume elements and show that the partition function so calculated is completely equivalent to the usual phase integral, provided that all degrees of freedom are classical and that anharmonicity and rotation-vibration interaction are neglected. Quantum corrections are also considered. The advantage of this form of the partition function lies in the fact that, for many applications, only quotients of partition functions are needed (e.g., for equilibrium constants). Thus a great deal of favorable cancellation may occur since the volume element for a given atom depends on its local environment. Applications to equilibrium constants for overall reaction and for transition state formation are carefully discussed by Herschbach *et al.*

Chemical kinetics.—Chemical reactions form a class of irreversible processes that have not been very much studied by the general methods of statistical mechanics. At one stage or another, most authors make some sort of equilibrium hypothesis, e.g., that the relative populations of molecular states have their equilibrium values. The validity of such a hypothesis for bimolecular gas phase reactions was examined some years ago by Prigogine *et al.* (149, 150) and by Curtiss (151). These authors found results that were very sensitive to the assumed energy dependence of the reaction cross section. Present (152) has re-examined the problem using a cross section he claims is more reasonable than those previously introduced. The technique

is to derive an expression for the perturbation of the Maxwell-Boltzmann distribution using the Maxwell equations of change rather than the Enskog integral equation approach, although the final formulae for the perturbation are the same as derived by Prigogine *et al.* When Present's cross section is inserted into his formula, one finds a rate differing from that predicted by simple collision theory by only 8 per cent for $\epsilon^*/kT = 5$, where ϵ^* is the threshold energy for the reaction, and by less for larger values of this ratio. In this calculation spherical symmetry of the reacting molecules was assumed, and steric factors, internal degrees of freedom, and heat of reaction were ignored. Subject to these limitations, the conclusion is that depletion of the high energy tail of the Maxwell distribution of velocities does not have a serious effect on the reaction rate.

Mahan (153) has performed a similar calculation using the methods of Prigogine. He investigated, however, the case of free radical reactions with essentially zero activation energy. In this case, which represents the opposite extreme from Present's calculation, he also finds that depletion of the tail of the Maxwell distribution has little effect on the reaction rate until the concentration of free radicals becomes appreciable, about 0.1 mole fraction in the example given.

A slightly different formalism has been used by Widom (154) to consider the case of collision induced dissociation of a more or less complex molecule imbedded in an inert gas. The basic formulation is in terms of a master equation rather than a Boltzmann equation. Instead of calculating a rate constant, Widom computes a mean first passage time, which is the mean time for the dissociation of a molecule, the reaction products being assumed removed from the system so that the recombination reaction does not occur. The inverse of this time is the rate constant whenever a rate constant exists. The mean first passage time is found for two models, and it is concluded that when the activation energy is much greater than kT , the equilibrium hypothesis is valid. This is in agreement with previously cited work.

A completely different approach is taken by Yamamoto (155), who considers bimolecular gas phase exchange reactions using the formalism of time correlation functions. Near to equilibrium, the reaction rate is proportional to the affinity, and Yamamoto expresses the proportionality factor as a time-temperature correlation function of the microscopic rate. An *ansatz* is made as to which regions of configuration space are to correspond to products and which to reactants, and the proportionality constant is then evaluated on the hypothesis of binary collisions. The rate constant can be determined from this proportionality constant, and it is assumed that the same rate constant will govern the reaction far from equilibrium as governs it near equilibrium. For a reaction $A + BC \rightleftharpoons AB + C$ Yamamoto finds the final result for the rate constant to be just that which would be given by the equilibrium hypothesis. In the course of the calculation, some relations among scattering amplitudes, of independent interest, are derived. However, certain of these relations,

which are written down without proof [Equations (3.21), (3.22), (3.23)], conflict with the well-known result that strict detailed balance does not hold for collisions of particles with internal degrees of freedom (156), hence this part of the paper needs further exposition and examination. Nevertheless, Yamamoto's work is quite important because it is the first application of the newer methods of irreversible statistical mechanics to chemical reactions.

There have been, of course, many other recent contributions to the theory of chemical kinetics, but these are more properly reviewed elsewhere. We have limited ourselves here to the discussion of articles we thought might be of interest at least as much for their statistical mechanical content as for their bearing on reaction rates.

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KINETICS OF THE SOLID STATE¹

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Most of the authors who have summarized the advances in solid state physics and chemistry in recent years have called attention to the overwhelming amount of effort being directed into this field, and have faced the choice of limiting their reviews to a few selected topics or of giving a synoptic discussion of the many papers that appear annually. The choice is a difficult one, and most have been content to make an admittedly arbitrary selection of those researches that interest them personally. This review is no exception, and its preoccupation with problems related to atom movements in crystalline solids reflects its author's chief interests. No apology is offered, since over the years the varying concerns of different reviewers accomplish a rather broad survey. Even within the more restricted area encompassed by kinetics of solid state processes, however, it is inevitable that only highlights can be touched, and many contributions must be arbitrarily left out of consideration.

An outstanding event of the year was the *Fourth International Symposium on the Reactivity of Solids*, held in Amsterdam, May 30 to June 4, 1960 under the auspices of the International Union of Pure and Applied Physics and the International Union of Pure and Applied Chemistry. Its organization, a miracle of efficiency and hospitality, was undertaken by the Royal Netherlands Chemical Society, the Netherlands Ceramic Society, and the Netherlands Physical Society. Reference to its Proceedings, shortly to be published, is frequent in this review.

POINT IMPERFECTIONS

Equilibrium lattice imperfections underlie many of the kinetic phenomena of solids, and their importance in diffusion, precipitation reactions, sintering, radiation damage, and oxidation of metals has long been known. Nevertheless, the direct measurement of the equilibrium concentration of point imperfections has been successfully accomplished only recently. The most reliable methods involve measurement of the excess resistivity of wires quenched rapidly from high temperatures, as pioneered by Koehler and his associates, or the comparison of the temperature-dependence of the lattice parameter with the thermal expansion. The former depends upon theoretical estimates of the electron scattering efficiency of vacancies. The latter, al-

¹ The survey of literature pertaining to this review was concluded in December, 1960.

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though it is an absolute method that is independent of lattice relaxation effects around vacancies, requires extraordinary precision in the measurement of both the lattice parameter and dilatation. Feder & Nowick (1) measured $\Delta a/a$ & $\Delta L/L$ for aluminum and obtained 3×10^{-4} at the melting point as the vacancy concentration

$$\left[\frac{\Delta N}{N} = 3 \left(\frac{\Delta L}{L} - \frac{\Delta a}{a} \right) \right] \text{ and } 0.77 \frac{\text{ev}}{\text{mole}}$$

for the energy of vacancy formation. Bradshaw & Pearson (2), using the resistivity-quench method, obtained $\Delta N/N = 6 \times 10^{-4}$ as the vacancy density at the melting point and 0.76 ev/mole for the formation energy. Simmons & Baluffi undertook the re-measurement for aluminum (3) and silver (4) by the diffraction-dilatometric method in a remarkably high precision study, finding $\Delta N/N = 9.4 \times 10^{-4}$ and 1.7×10^{-4} for aluminum and silver, respectively, at their melting points. The corresponding free energies for vacancy formation are 0.76 ev/mole and 1.09 ev/mole. Simmons & Baluffi (6), extending their studies on aluminum to quench-resistivity measurements, obtained 0.77 ev/mole for the vacancy formation energy. DeSorbo & Turnbull (7) obtained 0.65 ev/mole as the vacancy mobility energy from the annealing kinetics of the quenched-in resistivity of aluminum wires. The sum of the formation and mobility energies (1.42 ev/mole) is in good agreement with Spokas & Slichter's (8) value for the activation energy for self-diffusion in aluminum by nuclear magnetic resonance line width measurements. These excellent agreements encourage belief that the different methods are measuring the same property. Still unexplained, however, are the failure by both Feder & Nowick and by Van Duijn & Van Galen (5) to find any difference between the thermal expansion and lattice parameter change for lead.

Although the vacancy formation energies are in good agreement, there are discrepancies in the resistivity increment values found in the aluminum quench experiments that may be due to the loss of vacancies during quenching; these appear not to be caused by impurities, since DeSorbo & Turnbull (9) found the same $\Delta\rho$ increments for aluminum having widely different residual resistivity values. Bradshaw & Pearson (10) earlier had found little influence of purity on the resistivity increment in platinum.

In this connection, however, Damask & Dienes (11) have discussed the kinetics of vacancy annealing in terms of the binding energy of vacancies to impurity traps. Even though exponential decay of the excess resistivity is observed (and this is not always the case) it does not follow that the rate constant is related in a simple way to the vacancy mobility. By solving the non-linear coupled differential equations for vacancy annealing on an analog computer for such parameters as initial vacancy concentration, impurity concentration, and vacancy-impurity binding energy, they showed that the overall decay rate is not proportional to the vacancy mobility unless the impurity level is as low as 10^{-7} for reasonable estimates of the binding

energy. Although these considerations apply particularly to the determination of the mobility activation energy, it is clear that for large binding energies the equilibrium vacancy concentration itself (and hence the resistivity increment) may be impurity dependent. In a fast adiabatic microcalorimeter DeSorbo (12) measured the energy released in isothermal anneals of gold sheets that had been quenched from temperatures ranging from 820° to 920°C. The energy of formation of the quenched-in defects, presumed to be vacancies, was 0.97 ev/mole, in excellent agreement with Bauerle & Koehler's (13) value of 0.98 ± 0.03 ev/mole obtained from the annealing of resistance of quenched gold wires. From the rate of release of energy DeSorbo estimated the activation energy for defect motion, finding values that were temperature-dependent and ranged from 0.62 ev/mole at 920°C. to 0.73 ev/mole at 820°C. Bauerle & Koehler also found E_m to depend upon the quench temperature, and the results of the two groups are in substantial agreement. Using the calorimetric values for the energy of formation and the total energy released, DeSorbo estimated the vacancy volume to be 0.57 relative to the atomic volume of gold, in fair agreement with Tewordt's (14) theoretical estimate of 0.47 to 0.55 for vacancies in a *fcc* lattice. Extending the calorimetric technique to the isothermal aging of Al(Ag) alloys quenched from the homogenizing temperature, DeSorbo observed that more heat is released after a relatively slow quench than after a fast quench. These seemingly anomalous results, for which Borelius (15) had earlier defined two different states (ϵ' for the state produced by the slow quench and p_1 for the state produced by the rapid quench), were explained by means of Turnbull's (16) theory of cluster nucleation. In a quench of intermediate speed, vacancies may travel to normal sinks (dislocations and grain boundaries) during the low temperature anneal. Dislocation loops are formed at high quench rates, however, and their nucleation requires energy. Doyama & Koehler (17) quenched 2 mil diameter wires of 99.999 per cent silver and reported the formation energy of vacancies in silver to be 1.10 ± 0.04 ev/mole, in excellent agreement with Simmons and Baluffi's dilatometric-diffraction measurement quoted above (1.09 ± 0.10 ev/mole).

The question of the degree of relaxation of the lattice around vacancies, to which theoretical estimates ranging from essentially 0 to about 50 per cent in *fcc* structures have been reported, was taken up again by Girifalco & Weizer (18). Using a Morse potential function in a self-consistent calculation of the vacancy-directed relaxation in a cube of 20 atoms edge length they obtained the following percentage relaxations for first and second neighbors in *fcc* metals: Pb(1.42, -0.43), Ni(2.14, -0.39), Cu(2.24, -0.40), Ca(2.73, -0.41). For *bcc* metals it was necessary to consider relaxations out to the fourth nearest neighbor, with the following results: Fe(6.07, -2.12, -0.25, . . .), Ba(7.85, -2.70, 0.70, -0.33), Na(10.80, -3.14, 3.43, -0.20). The procedure followed was to partition the atoms into sets on spheres described about an interior atom of the cube. On removal of the central atom the position of minimum energy of the nearest shell atoms was calculated, holding

all other shells fixed. Using this as a first approximation for the nearest shell, it, and all but the second shell, were held fixed while the second shell atoms were allowed to take up their symmetrical location corresponding to minimum energy. The process was repeated for successive shells and then iterated until shell displacements were reduced below an arbitrarily small amount for the final configuration. The principal drawback to the calculation, of course, is that it fails to consider electron redistribution around the vacancy. In a similar calculation, Weizer & Girifalco (19) estimated the binding energy of divacancies as a function of their separation. With a Morse potential in a static lattice of copper atoms the force between vacancies is attractive at separations under 7 Å. Using 0.56 eV/mole as the vacancy relaxation energy obtained from the monovacancy relaxation calculations for copper, they found the stablest configuration for divacancies was for nearest neighbors, and the binding energy was estimated to be 0.64 eV/mole.

DIFFUSION

Dynamical theories.—Active interest in diffusion as one of the most important elementary processes in solids continues, but now that it is understood in broad outline there are efforts to clarify details as well as to make extensions to more complicated systems. Rice and his collaborators have elaborated further the dynamical approach to the theory of atom movements. In one paper (20) a simple model was chosen for purposes of calculation, consisting of an atom surrounded octahedrally by six nearest neighbors whose coupling to a hypothetical surrounding crystal is replaced by a set of adjusted constraints. Arbitrary but reasonable values of the bond force constants for the constrained "molecule" were selected; the central atom was then removed, and the frequency of the resultant vibrational mode in a direction 45 degrees from the bond axes was calculated for various altered force constants (normal mode frequencies). The frequency of this superposition mode, which corresponds in direction to a diffusive jump in a crystal and in magnitude to the jump frequency, was found to be quite insensitive to the choice of force constants, or to the presence or absence of the central atom. Significantly, anharmonic forces were found to arise that led to a large inward displacement of the shell atoms, corresponding to relaxation around a vacancy in a real crystal. How valid these conclusions may be when applied to a real crystal is conjectural, but the model calculation does serve to illustrate the physical significance of the dynamical theory of Rice in a particularly simple manner, and to emphasize that the anharmonic vibrational terms are responsible for relaxation effects.

In another model calculation, Plesner (21) analyzed the diffusive motion of an isotopic tracer atom in a linear lattice containing a vacancy. The Liouville equation in phase space was solved, taking into account the detailed interaction of the vibrational modes of the neighboring harmonic oscillators. A 6,12 potential was used with only nearest-neighbor interactions considered. The surprising conclusions (which are at variance with experi-

ment) are an inverse m^2 mass dependence of D and a fourth power dependence on the vacancy frequency. Manley & Rice (22) simplified the calculation of the frequency of occurrence of the diffusive configuration by noting that configurations in which shell atom displacements exceed the critical amplitude are of wholly negligible probability. Rice & Frisch (23), in an extension of the dynamical theory of diffusion, shed some light on the question of irreversibility in a diffusive jump by recognizing two time scales for the dissipation of energy, during the atom's flight across the barrier and during its captured state. Most of the energy loss of the moving atom occurs when the particle is captured, and is a consequence of the anharmonicity of the coupling of vibrational modes that are the means of de-excitation. Manley (24), using Rice's three conditions for defining the minimum requirements for atom jumps, proposed a simpler method of computing the probability for the simultaneous occurrence of the critical configuration in which the jumping atom reaches a sufficiently large displacement and simultaneously the shell atoms offer no lateral constraints. The calculation consists of two parts: (a) evaluating the limiting number of atom jumps for a fixed distribution of normal mode energies, and (b) computing the thermal average of that number, which is then identified with the probability of the critical configuration. Manley then showed the interesting correspondence of the dynamical theory with Zener's theory (25); the contribution to the activation energy that arises from the critical configuration probability is simply related to the elastic energy associated with the local deformation.

Volume of activation.—The volume of activation, defined in the reference terms of the activated state theory of diffusion,

$$\Delta V = -RT \left[\frac{\partial \ln \frac{D}{\gamma a^3 \nu}}{\partial P} \right] T,$$

continues to be a quantity whose experimentally derived values are hard to reconcile with a physical picture of the diffusive jump. Although the data are still meager, diffusion has been studied in a sufficient number of substances to conclude that the activation volume is invariably less than the gram-atomic volume. Like the energy of activation, the volume of activation and all other thermodynamic parameters of the activated state may be regarded as consisting of two terms: a formation term and a motion term. The mobility volume must be positive or zero for all diffusion mechanisms since it involves the outward displacement of the shell atoms, which usually impede the passage of the diffusing atom through its saddle configuration. The volume of formation of a sessile vacancy would be equal to the gram-atomic volume in the absence of lattice relaxation, and less than the gram-atomic volume if inward relaxation takes place. Most of the theoretical estimations of vacancy relaxation in *fcc* lattices, however, indicate little or no relaxation although a variety of approaches have been tried. [See, e.g., Kanzaki (26), Nardelli & Repanai (27), Huntington (28), Seeger & Bross (29), and Girifalco & Weizer

(18).] One would expect, on the basis of theoretical calculations, that the experimentally derived activation volume would equal or be larger than the gram-atomic volume. On the contrary, the writer and his colleagues reported activation volumes approximately 50 per cent of the gram-atomic volume for sodium and a correspondingly small value for α -white phosphorus. More recently Nachtrieb, Resing & Rice (30) reported the activation volume for lead self-diffusion to be at 13.0 cm^3 at 301°C ., with some evidence that it may be temperature-dependent. Tichelaar & Lazarus (31) measured the pressure-dependence of the anelastic relaxation in AgZn at 30 atom per cent zinc and calculated the activation volume to be 46 per cent of the atomic volume. Barnes, Engardt & Hultsch (32) interpreted their observed pressure-dependent nuclear magnetic resonance line narrowing in lithium metal to give an activation volume of 26 per cent of the gram-atomic volume. Only the calculations of Girifalco & Weizer (18) for *bcc* metals and Tewordt's (14) estimates for *fcc* metals give qualitative agreement with the experimental results. More experimental work and better models for theoretical calculations are clearly needed.

Keyes (33) has carefully re-examined the semi-empirical relationship between the volume of activation, the isothermal compressibility, and the activation energy; he has shown that the latter should be replaced by the Gibbs free energy of activation, since it is the latter quantity that represents (in the Wert—Zener theory) the isothermal reversible work performed by atoms against the elastic constraints of the lattice when they pass over the activation barrier. Keyes' relationship then becomes $\Delta V^\ddagger = k\beta\Delta G$, and since the compressibility is defined by

$$\beta = - \left(\frac{1}{V} \cdot \frac{\partial V}{\partial P} \right)_T$$

the equation may be written in integrated form as $\log \Delta G/\Delta G_0 = -k \log V/V_0$. Here it is important to distinguish between the activation volume ΔV^\ddagger , and the crystal volume V . Using Bridgman's data for the compressibility of sodium, Keyes re-analyzed the pressure-dependent sodium diffusion data of the author and colleagues (34) and obtained a remarkably good fit of the results for $k = 2.10$. Keyes' analysis is important because it allows for the variation of the volume of activation for substances in which the compressibility itself is a strong function of pressure.

Heitkamp (35) measured the pressure-dependence of the Kirkendall boundary marker shift in the indium-thallium system at pressures of 1, 3500, and 5400 atm. at 150° and 135°C . Marker shifts toward the thallium-rich (In-25 per cent Tl) and away from the thallium-poor (In-5 per cent Tl) alloys were observed, showing that indium is the more rapidly diffusing component. Pressure decreased the rate of marker displacement, and the effect was found to be larger than anticipated on the basis of concentration-independent self-diffusion coefficients. To within experimental error the marker displacements were proportional to $t^{1/2}$. Pressure evidently affects not merely

the atom mobility in this system, but the thermodynamic factor in the Darken equation as well.

Adda, Beyeler, Kirianenko & Pernot (36) studied the reactive diffusion of uranium with aluminum, copper, and nickel under both uniaxial and hydrostatic pressure. In these systems one or more intermetallic phases (often having non-stoichiometric compositions) are formed, and no complete interpretation is yet possible. The results are exceedingly interesting, nevertheless, and clearly show the increase in rate of interlayer growth as a function of pressure. The accelerated intergrowth rates, first thought attributable to plastic deformation under uniaxial stress, were confirmed in experiments under hydrostatic pressure. At atmospheric pressure there are composition gradients and concomitant gradients in lattice parameter within the product interphases; pressure has the effect of eliminating these gradients, which naively might have been thought to be driving forces for diffusion. In the uranium-aluminum system the range of composition is from $\text{UAl}_{2.2}$ to $\text{UAl}_{3.8}$ at low pressure, but becomes UAl_3 at 1000 atmospheres. The rate of increase of interlayer thickness in this system at 300°C . appears to be proportional to pressure and to increase by 400 per cent over the range 250 to 1000 atmospheres. The uranium-nickel system is more complex, the major interphase compound being UNi_5 , with layers of UNi_2 , U_5Ni_7 , and U_6Ni_9 . The intermetallic compound in the uranium-copper system is UCu_5 . By way of explanation of these effects, the possibility exists that very pronounced Kirkendall boundary shifts may be operative and these may destroy the interfacial contacts at low pressures. However, nothing is known about the influence of pressure on the phase diagrams of these systems nor of the diffusion mechanisms operating within the product compounds. More effort on these and related systems is likely to be rewarding.

Castleman (37) considered the effect of pressure on intermetallic layer growth in an idealized system of the uranium-aluminum type. For a case in which it is assumed that A and B interdiffuse at the same rate, volume changes are non-existent, and the growing interfaces are displaced equally and parabolically with time, he deduced a relationship that permits deciding whether the effect of pressure is primarily on the diffusivity or upon the interface concentrations. For the uranium-aluminum system it was not possible to explain the enhanced layer growth rate on the basis of pressure-induced changes in the equilibrium phase boundary concentrations.

Adda and co-workers have carried out an interesting series of studies on chemical diffusion in uranium alloys, making use of the Castaing electron micro-probe apparatus for measuring concentrations. Using tungsten wires and thin sheets of uranium and zirconium in stacked piles, Adda, Mairy & Andreu (38) measured boundary shifts as a function of concentration, and established that they are toward the uranium for concentrations ranging from 5 to 100 atom per cent uranium, and toward the zirconium for 0 to 5 atom per cent uranium in the γ -phase (950° to 1075°C .). Intrinsic diffusion coefficients for U and Zr were calculated by means of the Darken rela-

tions over the entire concentration range, and the ratio D_U/D_{Zr} is less than unity below 5 per cent U and greater than unity for all higher concentrations. Assuming that vacancies are present in equilibrium concentrations in the diffusion zone, the Darken equations lead to the following relationship between intrinsic and self-diffusion coefficients: $D_U/D_{Zr} = D_U^*/D_{Zr}^*$. Measurement of tracer self-diffusion coefficients for uranium and zirconium in a 5 atom per cent uranium alloy confirmed the expectation that $D_U < D_{Zr}$ below the concentration at which the boundary marker shift changes direction.

Adda & Philibert (39) studied intermetallic diffusion in the uranium-titanium system (γ -phase) by using the Castaing electron micro-probe for uranium concentrations between 0.05 and 0.9 atom per cent. Intrinsic diffusion coefficients were calculated from the Darken equations; uranium is the more rapidly moving component, and a significant Kirkendall effect was observed. The activation energies for uranium and titanium diffusion are 38.5 kcal./g.atom and 40 kcal./g.atom, respectively, and the ratio D_U/D_{Ti} is about 3.7 in the temperature range 950° to 1075°C. Bradley (40) measured the diffusion of sodium, potassium, and calcium in platinum by mass analysis of the ions that were thermionically emitted. Activation energies were estimated from $\log i$ versus $1/T$ curves for two different samples. The discrepancies (Na: 4.7, 5.3 ev, K: 4.4, 4.9 ev, Ca: 3.7, 4.5 ev) were presumed due to grain boundary or other structural causes. The activation energies are considerably higher than the activation energy reported by Kidson & Ross (41) for self-diffusion in platinum (2.96 ev) and still higher than the sum of the mobility and formation energies for vacancies in platinum measured by quench experiments by a number of investigators. [See, e.g., Lazarev & Ovcharenko (42), Bradshaw & Pearson (43), Ascoli, Asdente, Germagnoli & Manara (44), and Bacchella, Germagnoli & Granata (45), all of whom report $E_f + E_m$ values lying between 2.3 and 2.7 ev.] It seems evident that some process other than simple diffusion is being measured. A thermally activated process ascribed to the desorption of Na^+ and K^+ ions was also observed by Bradley when the platinum filaments were first subjected to rare gas ion bombardment at room temperature and then heated to thermionic emission. Plots of the logarithm of the characteristic time needed to reach the peak emission current versus $1/T$ gave values of 2.60 and 2.61 ev for sodium and 1.85 and 1.92 ev for potassium for the two platinum specimens. The differences in activation energy for the processes measured in the two experiments would then be a measure of the activation energy for volume diffusion of the impurities in platinum.

Adda, Kirianenko & Mairy (46) measured the rate of self-diffusion in β -uranium from 700° to 755° using couples made of natural and U^{234} -enriched uranium, and reported $D_0 = 1.35 \times 10^{-2}$ cm.² sec.⁻¹ and $Q = 42$ kcal./g.atom. An abrupt increase of more than two orders of magnitude in the diffusion coefficient occurs at the transformation from the β phase to the γ phase, and the activation energy drops to 27.5 kcal./g.atom in the latter. The results are ascribed to the covalent binding in β -uranium, with the higher energy of

vacancy formation in that phase. An interesting procedure was employed by Adda, Levy, Hadari & Tournier (47) for measuring the diffusion rate of strontium in uranium, and it may have application to other systems in which a volatile solute is sparingly soluble in the host lattice. The low solubility of strontium in uranium permits metallographic measurement of the time-dependent disappearance of strontium-rich precipitates at the interface between couples of pure uranium and the two-phase Sr-U alloy. Loss of strontium at the surface of the two-phase alloy is also dependent on the diffusion coefficient; therefore, comparison of the relative thicknesses of the strontium-depleted surface and interface zones permits a simple determination of D_{Sr} . So measured, D_{Sr} has an activation energy of 47 kcal./g.atom and $D_0 = 2.38 \text{ cm}^2 \text{ sec}^{-1}$. Inman & Barr (48) measured the diffusion of Sb^{124} in copper single crystals by a sectioning technique and reported $D = (0.34 \pm 0.12) \exp(-42,000 \pm 700/RT)$ for the temperature range 600° to 1000°C . Neither Lazarus' theory (49) nor its extension by Alfred & March (50) was in quantitative agreement with the results for $Q_{\text{Cu}} - Q_{\text{imp}}$, when the valence excess of antimony was taken to be +4. There appeared to be a better correlation of ΔQ with the diameter of the diffusing impurity: the larger d_{imp} , the smaller is ΔQ , presumably because the energy of vacancy formation is lowered in the vicinity of large atoms.

Diffusion in ionic crystals and semiconductors.—Although diffusion processes in metals formally have much in common with those occurring in ionic and covalent solids, there are notable differences: impurity-defect complexes may occur in all, but the introduction of a specified concentration of lattice vacancies by doping with aliovalent impurities has greatly aided interpretation of diffusion phenomena in ionic crystals. Use of the Nernst-Einstein relation with conductance and diffusion data has been a valuable means of demonstrating the existence of correlated atom movements (that lead to tracer-diffusion coefficients smaller than vacancy-diffusion coefficients) on the one hand, and of the diffusion of neutral anion-cation vacancy pairs on the other. Hanlon (51) measured the diffusion of cadmium ion in pure silver bromide and in silver bromide doped with cadmium bromide; in the latter each substitutional divalent cation introduces a vacancy in the cation sub-lattice. Over a range of Cd^{++} concentration from 0.23 to 3.30 atom per cent, Hanlon observed a tenfold increase in $D_{\text{Cd}^{++}}$, as compared with its rate in otherwise pure AgBr. The data supported Lidiard's theory (52), which postulates that a Cd^{++} ion uses a neighboring bound vacancy in its motion. The binding energy was estimated to be 0.21 eV for Cd^{++} -Ag vacancy complexes. High pressure measurements led to activation volumes of $9.8 \pm 1.0 \text{ cm}^3/\text{mole}$ for 0.54 per cent Cd and $8.1 \pm 1.0 \text{ cm}^3/\text{mole}$ for 3.30 per cent Cd; these are considered too small for an interstitial mechanism since two Ag^+ vacancies would be created for each interstitial Cd^{++} introduced. Direct interchange and ring mechanisms also appeared unlikely because the large concentration dependence that is observed would not be expected for such models. Laurance (53) studied the self-diffusion of Cl^{36} in

pure and CaCl_2 -doped sodium chloride. For pure NaCl he reported $D_{\text{Cl}^-} = 56 \exp(-2.12 \text{ eV}/kT)$, and for NaCl containing 0.01 to 0.1 mole per cent CaCl_2 , $D_{\text{Cl}^-} = 1280 \exp(-2.49 \text{ eV}/kT)$. Ca^{++} depressed D_{Cl^-} by a factor of 5 to 10, but most of the effect occurs for Ca^{++} concentrations below 0.01 mole per cent. Lidiard's theory again provided a qualitative explanation. Doping with Ca^{++} fixes the cation vacancy concentration and the single anion vacancy concentration must therefore decrease rapidly with temperature according to the mass action law: $n_+ \cdot n_- = N^2 \exp(-E_f/kT)$. If the chloride ions were to diffuse by making use of single Cl^- vacancies their diffusion coefficient would decrease about two orders of magnitude more than was observed over the concentration range studied. On the other hand, if chloride ions diffuse by means of anion divacancies in accordance with Lidiard's theory, there should be no dependence on the Ca^{++} concentration. However, since D_{Cl^-} is depressed approximately an order of magnitude by small Ca^{++} concentrations, anion vacancy pair diffusion is not the only mechanism. Laurance suggested that single anion vacancies are responsible for Cl^- diffusion at low cation doping levels, and that the Lidiard mechanism is operative at higher concentrations of calcium. Lynch's (54) measurements of cation and anion tracer diffusion in CsBr and CsI showed that for both salts the anion diffuses with lower activation energy than the cation. Diffusion of Cs^+ followed the Arrhenius rate expression over the entire temperature range, but in both salts the halide ions displayed a temperature-dependent activation energy. Lynch postulated that in addition to the Schottky mechanism for cations and anions which dominates at high temperatures, a conductivity-independent anion mechanism exists at lower temperatures; the Zener ring diffusion mechanism in the halide sub-lattice is a possibility. Transport number experiments by Laurance (55) in cesium bromide were carried out using the Tubandt method. Complications arose that were associated with intergrowths at the interfaces between the CsBr crystals. Depressions on the crystal junctions facing the cathode indicated selective impediment of the transport of bromide ion across the boundary. Applying the usual Tubandt analysis led to a transport number of 0.49 for Cs^+ , but this value may be too large if Br^- cannot traverse the crystal junctions without special activation.

Oishi & Kingery (56) measured the rate of self-diffusion of oxygen in single crystal and polycrystalline Al_2O_3 from the exchange of oxygen between $\text{Al}_2\text{O}_3^{16}$ and O_2 enriched with the mass 18 isotope. In Al_2O_3 from crushed single crystals the diffusion coefficient was given by $D = 1.9 \times 10^3 \exp(-152,000 \pm 25,000/kT)$ above 1600°C . At lower temperatures the results were variable and dependent upon impurities and previous heat treatment. The diffusion coefficient is about 100-fold larger in polycrystalline Al_2O_3 over the temperature range studied, and the energy of activation is lower. From the single crystal experiments the energy of formation of Schottky pairs (O^- and $\frac{2}{3} \text{Al}^{3+}$) was calculated to be 157 kcal./mole. The same method was applied (57) to measure the diffusion coefficient of oxygen in periclase (MgO) from 1300° to 1750°C . The results are given by $D = 2.5 \times 10^{-6}$

exp $(-62,400/RT)$, but are believed to be impurity-controlled because the pre-exponential term is so small. Haas (58) made calculations of the rate of diffusion of oxygen in silicon and germanium, based upon the acoustical damping experiments of Southgate (59). The calculations assumed that oxygen forms bonds of the type Si—O—Si and when one bond is broken it may be re-formed on any one of six neighboring Si—Si bonds in a rapid uncorrelated motion. The diffusion coefficient is then given by $D = \Delta^2/\tau$, where $1/\tau$ is the resonance absorption frequency and Δ is related to the Si—Si distance, a , by $\Delta = a(\frac{1}{3})^{1/2}$. It then follows that $D = \frac{1}{3} \cdot a^2/\tau \exp(-Q/kT)$. For silicon $D_0 = 0.21 \text{ cm}^2 \text{ sec}^{-1}$ and $Q = 2.55 \text{ ev/g.atom}$, while for germanium $D_0 = 0.17 \text{ cm}^2 \text{ sec}^{-1}$ and $Q = 2.02 \text{ ev/g.atom}$. The analysis shows that for the internal friction measurements with the stress along the $\langle 111 \rangle$ direction, the six oxygen positions are not equivalent, and exchange among them will lead to damping. Along the $\langle 100 \rangle$ direction all six positions are equivalent, and no resonance absorption should be expected. Southgate's experiments confirmed these expectations. Reasonable agreement was found with the diffusion experiments of Logan & Peters (60), based on the conversion of p -type silicon to n -type by oxidation at 1300°C . ($1.0 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$ as compared with $1.4 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$ from calculations based on internal friction).

Pell (61, 62) used several interesting methods for measuring the diffusion coefficient of lithium in silicon at high and low temperatures. Lithium was first diffused into silicon until its concentration (below the extrinsic level) was essentially uniform. It was then out-diffused, and the maximum concentration in the center of the specimen was determined as a function of time by measuring the conductance or the effective Hall constant. D was evaluated from an appropriate solution to the differential equation for the sample geometry and boundary conditions, and its temperature dependence was found to follow the equation $D = (2.5 \pm 0.2) \times 10^{-3} \exp(-0.655 \pm 0.01 \text{ ev}/kT)$ from 800° to 1350°C . This is in excellent agreement with the results of Fuller & Severiens (63) in the lower temperature interval, 360° to 860°C ., and supports the belief that the diffusing species is the Li^+ ion. The question of the nature of the potential barrier that the Li^+ ion surmounts in a diffusive jump was considered from the standpoint of Zener's elastic strain energy model, polarization of Si atoms by Li^+ ions, and electrostatic interaction of Li^+ ion with the periodic potential of the lattice, and the latter was considered to be the most probable. For temperatures ranging from room temperature to 125°C . Pell determined D_{Li^+} in silicon from the time decay of the capacitance of a p - n junction that had been reverse-biased, and toward which Li^+ ions drift. The same equation found for high temperatures applied in the low range, and describes the process over eight orders of magnitude in D . Shashkov & Akimchenko (64) also studied the diffusion of lithium in silicon from 400° to 800°C . by measuring the depth of the p - n junction formed when lithium metal was diffused into p -type germanium. The junction depth was measured microscopically after etching with HNO_3 or by locating it with barium titanate. Single crystals of differing resistivity and dislocation

density, and crystals with twins oriented both parallel and perpendicular to the diffusion direction, all gave results that lay on the same $\log D$ versus $1/T$ plot, showing the structural insensitivity of the process. The diffusion coefficient was given by $D = 2.2 \times 10^{-3} \exp(-16,200/RT)$, which is in good agreement with Pell's results. Potemkin, Potapov & Petrov (65) studied the electromigration of copper in germanium and concluded that the copper species is a negative ion in the temperature range 500° to 680°C. This is in accord with the results of Severiens & Fuller (66), who found that the copper becomes a neutral species at 700°C., and in disagreement with the conclusions of Boltaks (67), who claimed that copper is neutral in the range 500° to 700°C. At temperatures above 800°C. there is agreement that copper is positively charged in germanium. Allen (68) discussed the concentration-dependence of the diffusion rate of impurities in semiconductors. The Fermi level lies in the valence band if the concentration of acceptor impurities is high, and most of the impurities do not accept electrons. As the impurity concentration decreases, the Fermi level rises and an increasing fraction of the impurities accept electrons. Two impurity states are postulated (ionized and un-ionized) having different interaction energies with the crystal field and correspondingly different impurity diffusion coefficients. Fick's Law accordingly becomes

$$\frac{dN_I}{dt} = \frac{\partial}{\partial x} \left(D_i \cdot \frac{\partial N_i}{\partial x} + D_u \cdot \frac{\partial N_u}{\partial x} \right)$$

where the subscripts i and u denote "ionized" and "un-ionized," and the total impurity atom fraction is $N_I = N_i + N_u$. On this theory one would expect to find penetration profiles showing rather abrupt changes in slope with distance as the impurity concentration and degree of ionization vary. Such a state of affairs is proposed to account for the anomalous results obtained by Cunnell & Gooch (69) for the diffusion of zinc into gallium arsenide. Zinc diffusing into gallium arsenide from the vapor should conform to the complementary error function solution to the diffusion equation, but deviates widely therefrom. D_{Zn} appears to be large near the surface of the crystal and to decrease greatly with increasing depth. In accordance with Allen's theory, it is suggested that un-ionized zinc atoms diffuse rapidly into gallium arsenide near the crystal surface, and that as their concentration falls below the critical level in the interior they become negative species with slow diffusion characteristics. This is a particularly complicated system, inasmuch as the vapor pressure of arsenic is high. The mass action law requires that the product of the vacancy concentrations in the gallium and arsenic sub-lattices be constant, and the observed dependence of D_{Zn} upon the partial pressure of arsenic indicates that there is a complicated interaction of impurity atoms, vacancies and electrons.

The anisotropic diffusion of copper into Bi_2Te_3 was studied by Carlson (70), who observed rapid diffusion parallel to the layer planes of the rhombohedral lattice and slow diffusion in the perpendicular direction ($\langle 111 \rangle$). In

the (111) direction the sequence of atoms is . . . Te-Bi-Te-Bi-Te---Te-Bi-Te-Bi-Te---Te-, with only weak electrostatic forces operating between adjacent tellurium layers. Cu⁶⁴ is believed to diffuse with low activation energy between the Te layers [$D_{//} = 0.0034 \exp(-0.21 \text{ eV}/kT)$] and with high activation energy in the perpendicular direction [$D_{\perp} = 0.071 \exp(-0.80 \text{ eV}/kT)$] where there are stronger ionic and covalent forces. Bi₂Te₃ is ordinarily a *p*-type semiconductor. Copper converts it into an *n*-type semiconductor, but the material becomes less *n*-type after standing at room temperature, and copper is observed to diffuse to the surface.

Sandulova & Yu-Liang (71) found that diffusion of Ta¹⁸² into germanium depended strongly upon the carrier type and crystal perfection. High purity *p*-type germanium (60 ohm cm. resistivity) had an activation energy of 65 kcal./g.atom, while low purity (0.5 to 1 ohm cm.) material had an activation energy of only 19.4 kcal./g.atom. It was concluded that tantalum probably diffuses substitutionally. Like many other solutes in germanium, tantalum displays retrograde solubility with a maximum of about 4×10^{19} atoms/cm.³ at 880°C., independent of carrier type.

Diffusion in a thermal gradient (Soret effect).—Interest in Soret diffusion as a possible means of understanding the localization of the activation energy in terms of the heat of transport has produced several experimental and theoretical researches. Allnatt & Rice (72) analyzed the diffusive motion of atoms in a thermal gradient by an extension of the dynamical theory, and they concluded with LeClaire (73) that the energy of activation for motion is precisely equal to the heat of transport (i.e., the heat that must be supplied to the initial site to maintain local isothermal equilibrium). This is in disagreement with Wirtz (74), who interpreted the heat of transport as the energy required to prepare the lattice around the final site to receive the jumping atom. Shewmon (75) obtained -24.5 ± 1.5 kcal./g.atom as the heat of transport for the interstitial diffusion of carbon in α -iron at 700°C. The flux of atoms in a combined thermal and concentration gradient is given by Fick's Law, modified to read:

$$J_i = \frac{-D_i N_i}{RT} \left[\left(\frac{\partial \mu_i}{\partial x} \right)_T + \frac{Q^*}{T} \frac{dT}{dx} \right].$$

In the steady state, when the flux due to the thermal and concentration gradients has reduced to zero, the equation may be solved for the heat of transport:

$$Q^* = -T \frac{dx}{dT} \left(\frac{\partial \mu_i}{\partial x} \right)_T.$$

To a satisfactory approximation, Q^* is then simply the slope of $-R \ln N_i$ versus $1/T$.

Brammer (76) looked for platinum marker shifts in α -iron at 900° in a temperature gradient of 2500°/cm. Assuming the activation energy for motion to be $0.35E_d$ a marker displacement of 0.001" was expected, but no

shifts were observed beyond the uncertainty of measurement (0.0001"). He concluded that either a vacancy mechanism is not operative in α -iron or else that the mobility and formation energies of vacancies must be equal ($E_f = E_m = 0.5E_d$).

IRRADIATION EFFECTS IN SOLIDS

Irradiation studies of solids by high energy particles, initially of interest for the undesirable effects produced on structural properties, have become increasingly important for the information they may yield on the defect structures of solids and for the influence they have on rate processes. A number of aspects of radiation-induced kinetic effects were discussed at the *Fourth International Symposium on the Reactivity of Solids* in Amsterdam. Dienes (77) reviewed the fundamentals of high energy particle encounters with lattice atoms leading to the production of simple defects, clusters, and thermal spikes and then called attention to the chemical effects of radiation damage. Enhanced oxidation rates in graphite, increased rates of reduction of nickel oxide by hydrogen, and increased solution rates of Fe_2O_3 in acids are among the kinetic effects caused by neutron and proton irradiation. Catalytic effects of solids in heterogeneous reactions (e.g., *ortho-para* hydrogen exchange and H_2 - D_2 exchange rates) are augmented by γ -radiation. The kinetic effects are often difficult to reproduce quantitatively and the detailed causes are little understood. For this reason, recent studies have emphasized the effects of radiation on physical and chemical adsorption. Neutron irradiation of Al_2O_3 increases the energy of adsorption of argon, presumably by diminishing the density of low energy sites and increasing the concentration of high energy sites. Similarly, the up-take of hydrogen on irradiated Al_2O_3 is diminished, but the molecules that are adsorbed are more firmly bound. Riehl & Marth (78) reported studies of the surface changes produced in metals by alpha particles and recoil atoms. Electron microscope techniques failed to reveal the displacement spikes and craters expected to form when recoil atoms impinge upon metal surfaces. On the contrary, irradiation causes a smoothing of metal surfaces, probably by forming mobile interstitial atoms that readily diffuse to surface irregularities. Spilners & Smoluchowski (79) described the changes caused in the kinetics of formic acid decomposition on proton-irradiated copper sheets. The rates and activation energy for the zero order decomposition to CO_2 and H_2O are lowered, and it is proposed that catalytically active sites on the metal are reduced in number by the increased surface mobilities of metal atoms. The remaining catalytic sites, which may be strained regions of the metal surface in the vicinity of emerging dislocations, are catalytically more active than the radiation-healed sites. Cox (80) summarized the work at Harwell on the kinetics of zirconium oxidation which is accelerated by neutron and fission fragment irradiation. The chief cause of the accelerated oxidation rate appears to be fission fragment tracks produced in the oxide film, which are not annealed at the temperatures employed. These provide diffusion paths for the transport of reactive species to the metal-oxide interface. Clark & Palmer (81) studied

the annealing of 2 Mev electron damage to diamonds by following the changes in the absorption spectra. The annealing data for the 6200 Å band, thought to be attributable to vacancies, show that a wide range of processes with different activation energies is involved. Damask (82) discussed the radiation-enhanced annealing of frozen-in short range disorder in α -brass. At 50°C. electron irradiation was shown by resistivity measurements to reduce the free energy to its minimum in a few hours, although it would require about 30,000 years to accomplish the same ordering by thermal fluctuations. Radiation can also cause hardening in metals, as Makin & Minter (83) demonstrated in neutron irradiations of copper and nickel wires. Tensile tests revealed two types of radiation hardening: source hardening, which inhibits the nucleation of slip; and lattice hardening, which impedes the propagation of slip. The results on as-irradiated specimens confirmed the general features of Seeger's theory (84), but indicated that the assumption of a constant activation energy is an over-simplification. Gray & Cummings (85) measured both the change in lattice parameter and the microhardness of molybdenum irradiated with fast neutrons, and concluded that interstitial atoms are produced that are mobile at room temperature. Below a critical dosage (10^{19} neutrons/cm.²) the principal recovery mechanism seems to be a recombination of interstitials with vacancies and trapping at small substitutional impurity atoms. For high level exposures the interstitials form clusters that grow in size with continued aging. Cuypers & Amelinckx (86) used 40 kv x-radiation to study the surface hardening of sodium chloride crystals at room temperature. Vacancy clusters are believed responsible for the hardening. Isothermal anneals in the temperature range 150° to 300°C. cause re-softening. Below 200° the re-softening is caused by the growth of vacancy clusters to larger size, with a consequent decrease in number. Above 200° the crystal density increases and vacancy clusters are believed to dissociate and disappear. Above 300° the hardness is restored to its un-irradiated value. Although the annealing kinetics follow a first order rate law and the Arrhenius plot is linear with an apparent activation energy of 0.19 ev/mole, the process is believed to be the superposition of many stages whose overall rate is fortuitously first order. One of the most promising attempts to understand the fundamentals of interactions between high energy particles with lattice atoms is being followed by Gibson, Goland, Milgram & Vineyard (87) at the Brookhaven National Laboratory. Preliminary machine calculations have been made on a model of the *fcc* lattice of atoms bound by two-body central forces with a Born-Mayer potential. Constant surface forces were chosen to simulate the bonding due to conduction electrons, and the "crystallites" consisted of 500 to 1000 atoms. The procedure followed was to allow a given atom to acquire a high energy with its velocity along a chosen direction, as though it had been struck by a high energy particle. The equations of motion of all the atoms in the ensemble are then solved as the hot atom dissipates its energy, and the atom configurations of the damaged crystallite are examined when the excess kinetic energy is lost. Some of the more interesting and important conclusions are: (a) low energy damage produces vacancies and

interstitials, (b) vacancies are normal in configuration but the stablest configuration for interstitials is a pair, symmetrically displaced about a lattice site, (c) collision chains that produce simple atom replacements and do not damage the structure occur in the $\langle 110 \rangle$ and $\langle 100 \rangle$ directions with low energy losses in the former, (d) above 25 to 30 ev, chains transport matter as well as energy, producing a terminal interstitial far from the collision site, (e) vacancies remain near the site in compact groups and form cluster patterns at moderate energies, (f) collision chains produce many more replacements than displacements, (g) the threshold energy for Frenkel pairs is about 25 ev in the $\langle 110 \rangle$ or $\langle 100 \rangle$ directions and about 85 ev in the $\langle 111 \rangle$ directions, (h) close Frenkel pairs along the $\langle 110 \rangle$ directions are unstable and must be fourth nearest neighbors, or more remote, for stability. The possibilities of further clarifying the nature of the defects produced are great, as the many variables are systematically coded into problems. Lambe (88) introduced minute traces of impurity atoms into solid neon and krypton by radioactive decay of incorporated tritium and Kr^{86} and examined the solids for electron paramagnetic resonance absorption at 4.2°K. Atomic tritium formed in the tritium decay ($\text{H}_2^3 \xrightarrow{\beta} \text{He}^3 + \text{H}^3$) was found to behave as an almost free atom in neon, but no $(\text{He}^3)^+$ was found. The Rb^{86} which should have formed in solid krypton by decay of Kr^{86} was not found either. In selected cases this should be a useful method for exploring the binding effects of impurities in solids at very low concentrations.

SOLID STATE REACTIONS

Homogeneous reactions.—The chemical reactions involving solids may be broadly classified as either homogeneous or heterogeneous. The first includes such phenomena as the nucleation of new phases from solid solution, as well as diffusion-controlled association phenomena involving charged species in ionic and semiconducting solids, and the thermal annealing of defects induced by radiation or quenching. Heterogeneous reactions cover a much wider range of possibilities, but are most commonly associated with the oxidation of metals or the converse reduction of oxides by gases or solids, the growth and dissolution of crystals, phase transformations, the growth of precipitates, and the decomposition of compounds. Not infrequently, as in nucleation and growth, homogeneous and heterogeneous reactions are closely linked. Rate laws in which the product layer thickness varies according to the square root of time (parabolic) are most common, although linear, cubic, and logarithmic rate laws are well-known. Even though it is often possible to characterize a reaction according to a particular rate law, the detailed elucidation of the mechanism may be obscure. In other cases the rate constant may be time-dependent. Waite (89) has discussed bimolecular reaction kinetics in solids and liquids in which simple second order kinetics are not followed. A general reaction rate equation was developed in which the order is two, but the rate constant is a function of time. Three parameters are involved: D , the sum of the diffusion coefficients of the reacting species; r_0 , their capture radius; and s , the ratio of the probability that two species

will react when separated by the capture radius to the probability that they will diffuse apart before reacting. Turnbull, Rosenbaum & Treatise (90) studied the rapid clustering reaction of copper, aluminum, and silver in alloys of these metals with aluminum after rapid quenches from the homogenizing temperature. Precipitation occurs at 200° to 300°K., and the clusters may contain 100 or fewer atoms (10^{18} clusters per cm.³). The reaction is essentially independent of solute concentration, and is interpreted as arising from the quenching-in of vacancies (*vide supra*) that, in their annealing at low temperatures, enhance solute mobilities. At very high vacancy concentrations dislocation loops are probably formed by vacancy aggregation. If the quench is briefly interrupted at 333° to 498°K. the clustering rate is greatly reduced, presumably by forming dislocation loops that short-circuit the solute diffusion.

Kaufman, Leyenaar & Harvey (91) discussed the effect of pressure on the lowering of the martensitic transformation temperature (M_s). There is a bulk thermodynamic effect of hydrostatic pressure that stabilizes the *fcc* austenite relative to *bcc* martensite. Over and beyond this, however, pressure "freezes-in" the martensitic embryos with smaller-than-critical radii and a larger free energy difference $\Delta F_\gamma - \Delta F_\alpha$ (lower temperature) is needed for the transformation to occur. Ubbelohde (92) called attention to hysteresis phenomena in certain allotropic phase transformations, in which the structures of the two phases differ only slightly. Hybrid crystals may form in which both structures may coexist during thermal cycling through the transition temperature. Perfect single crystals may be formed from such hybrids. Ubbelohde believes that variables other than free energy, pressure, and temperature are needed to describe the transformations for such structurally related allotropes, and suggests that strain energy and internal surface energy terms must be included in the free energy. Dachille & Roy (93) described the effect of "displacive-shearing" stresses on transformations. Laboratory grinders and mixers may convert PbO_2 , MnF_2 , $CaCO_3$, and BeF_2 into their high pressure modifications, which would require up to 10,000 atmospheres under equilibrium conditions at room temperature. Shear stresses can increase reaction rates by as much as two or three orders of magnitude, but it is not known whether the cause is stored strain energy or increased reactivity due to bond rupture. Cohen & Schmidt (94) discussed the structure-sensitivity of certain photochemical reactions in organic crystals, such as the dimerization of acrylic acids.

Small concentrations of copper or silver in zinc sulfide form nuclei of cuprous sulfide or silver sulfide that trigger the transformation from wurtzite (*hcp*) to sphalerite (*fcc*). Avén & Parodi (95) studied the transformation at several temperatures by means of electron paramagnetic resonance, using traces of Mn^{+2} in the zinc sulfide as an indicator for the extent of transformation. In a cubic field (sphalerite) Mn^{+2} shows six equally spaced resonance lines, while in wurtzite there are more than thirty lines. The energy release on precipitation of the copper or silver sulfide nuclei supplies the energy for nucleating the sphalerite phase.

Heterogeneous reactions.—Smeltzer (96) studied the kinetics of scale formation on iron from 600° to 1100°C. in carbon dioxide using a thermogravimetric method, and he identified the oxides by x-ray and microscopic examinations. The oxidation rate was linear for short times but followed a parabolic law for longer times. The linear rate resulted from the incorporation of chemisorbed oxygen into wüstite (FeO) below 910°C. and by the dissociation of CO₂ and incorporation of oxygen at higher temperatures. Below the Curie point both wüstite and magnetite formed, but above this temperature only wüstite was produced. Fuller (97) used the impurities (NiO, CuO, CoO) in iron as boundary markers to study the mechanism of oxidation of wüstite to magnetite. Armco iron, oxidized to FeO, has a layer of impurity oxides on its surface that do not dissolve in FeO or Fe₃O₄. Removal of the FeO layer from the metal and subsequent oxidation in steam and air at 600° to 1200°C. leaves the impurity markers imbedded within the Fe₃O₄ at a definite fractional distance below the atmosphere-oxide interface. Fe₃O₄ below the boundary markers is produced by the reaction $4\text{FeO} = \text{Fe} + \text{Fe}_3\text{O}_4$. Fe₃O₄ above the impurity oxides is formed from the diffusion of iron through the Fe₃O₄ to the oxide-atmosphere interface, where the reaction $\text{Fe} + \frac{3}{2}\text{O}_2 = \frac{1}{3}\text{Fe}_3\text{O}_4$ occurs. The relative thickness of the Fe₃O₄ layer therefore should be 1:4 if iron and not an oxygen species is the mobile component. Experimentally the ratio is found to be 4.27. Pettit, Yinger & Wagner (98) studied the oxidation of iron to wüstite from 925° to 1075° in carbon monoxide-carbon dioxide mixtures. The results confirm Wagner's mechanism that the rate determining step is the formation of adsorbed oxygen by the reaction: $\text{CO}_{2(g)} = \text{CO}_{(g)} + \text{O}_{\text{ads.}}$

Ligenza & Spitzer (99) grew films of amorphous SiO₂ on silicon by high temperature oxidation in steam or oxygen using O¹⁸-enriched sources. The mechanism of SiO₂ film formation could be followed by observing the infrared absorption bands, which were shifted to longer wavelengths by the O¹⁸ isotope. By forming an oxide film with one oxygen isotope and continuing its growth with the other isotope it was found that silicon atoms do not diffuse through the oxide layer. On the contrary, the mobile oxygen species (from O₂ or H₂O) diffuses through the oxide layer and forms new oxide at the Si-SiO₂ interface. In steam there is quite complete oxygen exchange, as shown by experiments in which SiO₂¹⁶ was converted to SiO₂¹⁸ by D₂O¹⁸. In steam the oxidation rate is not time dependent, and is proportional to the partial pressure of water vapor; the activation energy is 23 kcal./mole. In oxygen the rate is proportional to $(p_{\text{O}_2})^{4/5}$, and is inversely proportional to the film thickness; the activation energy in oxygen is 40 kcal./mole.

Gallagher & Anderson (100) considered various mechanisms of gas-solid reactions and derived the logarithmic rate law by considering the distribution of reactive sites having different activation energies. Bennet & Tompkins (101) reviewed the oxidation of germanium, and provided data on the chemisorption of oxygen atoms. The change in surface electrical potential on adsorption and desorption is in agreement with theory.

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SURFACE CATALYSIS¹

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This essay must be essentially eclectic in nature, highly personal, with a selection of a limited number of topics in the subject of catalysis at solid surfaces, chosen because of their special interest to the writer of the article.

It has been a banner year in the recording of catalytic developments with several congresses, both national and international; at least two new journals devoted to publications in the field of chemical kinetics and catalysis; the completion, with Volume 7, of the *Handbook of Catalysis* of which Paul H. Emmett has been the distinguished editor (1); and a further volume, XII, of *Advances in Catalysis* (2). In addition to the usual Gordon Conference which, this year, glanced back at the Second International Congress held in July in Paris, there was also a two-day symposium held at the American Chemical Society's September meeting in New York, where various aspects of important modern catalytic research came under discussion.

As to the Congress, between Monday and Friday, July 4-8, 1960, some 117 papers were presented to three working sections that often met simultaneously. Although the sections met in the same building, the Maison de la Chimie, the conflicts in the schedules frequently made it impossible for a listener to attend two or even three topics in which he was interested, by reason of their simultaneous presentation. It would have required a well-coordinated team of three to cover the proceedings adequately. Any version by a single person must necessarily be fragmentary. The Proceedings are to be published in three volumes, it is said. The sections were concerned primarily with (a) kinetics and mechanism, (b) physicochemical properties of catalysts and catalytic activity, and (c) applied catalysis. At the opening meeting, after the usual welcomes, the three section reporters, Kemball, Schwab, and Haensel outlined the main features of the contributions to their several sections, details of which will, in part, be presented in subsequent pages.

The opening address was made by the president, M. Prettre; three formal lectures were presented by Professor G. Natta on *Stereospecific Catalysis*, by Professors N. N. Semenov and V. V. Voevodsky on *Chain Reactions*, and by Dr. H. Heinemann on the *Relationships between Basic Research and Applied Research* in the field of catalysis; and a closing session included the coverage of enzymatic catalysis by Professor H. Theorell and trends in industrial catalysis by Dr. E. Houdry, as well as a closing address by the writer.

¹ The survey of literature pertaining to this review was concluded in December 1960.

A national symposium of high distinction was held by Dutch scientists in Amsterdam in mid-November 1959 and was available in English, edited by J. H. De Boer *et al.*, by mid-1960 (3). Of this publication I can repeat some earlier remarks (4).

Anyone who wishes to learn the main features of current aspects of heterogeneous catalysis as to mechanism, electronic and chemical factors in heterogeneous catalytic change in gas phase or solution, with decomposition of formic acid or synthesis of ammonia as examples, of Ziegler catalysts, selective hydrogenation and finally bifunctional catalysis cannot do better than purchase the brief volume of 180 pages.

Late in 1959 a new journal, *Shokubui* (Catalyst), to be published several times a year, was announced by the Catalysis Club of Japan. The journal was launched by Professor J. Horiuti, President, and Vice Presidents T. Shiba and T. Yatagaya. On behalf of American workers in catalysis, I sent a message of congratulation to Professor Horiuti on the new venture. The contents are printed in Japanese. It is to be hoped that an extensive summary of each article in some Western language will accompany its publication. Japanese effort in catalysis in recent years has been an important factor in the progress of the subject.

Volume 1, No. 1, of a new Russian journal *Kinetika i Kataliz*, with Professor G. K. Boreskov as Editor, appeared in May-June 1960. Copies were distributed by the Editor to participants in the Second International Congress on Catalysis in Paris, July 1960. It contained an English table of contents but, unfortunately, no English abstracts of the papers, as has been customary in several Soviet journals. The first papers were frequently of a review nature concerning information that has appeared elsewhere in the Soviet literature. Most of them are first-class, and a second number of the first volume, recently received in U.S.A., indicates that the new journal may add to the significant role of Soviet science in the development of catalysis. This new journal is one of six now being published by the Siberian Division of the Academy of Science, U.S.S.R. It will be nurtured by new Institutes for Catalysis, Kinetics and Combustion, Organic Chemistry, Inorganic Chemistry, etc., that have recently sprung up in the area of Novosibirsk. Top scientists from Moscow, among them Professor Boreskov, Head of the new Institute for Catalysis, and Dr. Voevodsky, Head of the new Institute for Kinetics and Combustion, are taking with them numerous Russian scientists and technicians in this trek eastward from Russia proper. In the preface to the first issue of this journal it is acknowledged that an investment of 10¹¹ roubles between 1959 and 1965 will be involved in this major development of the chemical industry. Limited knowledge of chemical reactivity and associated chemical engineering problems are regarded as major obstacles to be overcome in the interest of more rapid progress.

It will be useful before proceeding to the special sections of this annual review to summarize the several chapters in Volume XII of the *Advances in Catalysis* (2) since these will not be discussed in the subsequent sections of

this report. In Chapter 1, Grimley discusses the wave mechanics of the surface bond in chemisorption. He is concerned with the nature of the bond formed when an atom or molecule is adsorbed on to the surface of a solid. The difficulties inherent in this problem emerge from the treatment. Chapter 2 deals with magnetic resonance techniques in catalytic research. Both nuclear magnetic resonance and electron paramagnetic resonance are included in the discussion. Base-catalysed reactions of hydrocarbons in contrast with the more-studied acid catalysed processes are discussed in Chapter 3. In Chapter 4 a technique known to physicists for more than thirty years but only now being applied to catalytically active solids is considered. The use of x-ray K-absorption edges in the study of catalysts is shown, after review of the basic theory, in its application to such spectra as those of manganese, cobalt, chromium, titanium, nickel oxides, and compounds. In respect to catalysts it was found, for example, in the examination of some supported chromia catalysts, that "a pronounced variation in catalyst performance, caused by certain oxidative pretreatments, was found to correlate with variations in absorption edge spectra." The ability of x-rays to penetrate matter, such as reactor windows, catalyst supports, and catalyst deposits is one illustration of the features making x-ray K-edge spectroscopy especially attractive for catalyst investigations. The electron-theory of catalysis on semi-conductors is comprehensively treated in Chapter 5 by Th. Wolkenstein of the Institute of Physical Chemistry of the Academy of Sciences, U.S.S.R., in Moscow. It is especially advantageous to have this exposition in English by one of the pioneers in the electron theory now so widely discussed, as will emerge subsequently, in present day considerations of catalysis. A final chapter on Molecular Specificity in Physical Adsorption by D. Y. C. Yates, formerly of Cambridge, now at the School of Mines, Columbia University, New York, emphasizes that, even in physical adsorption, there are perturbations both in the adsorbing solids and in the adsorbed gases during the process. Early work by Bangham and his co-workers in the two decades from the 1920's to the 1940's here receives an up-to-date, modern, and comprehensive treatment.

FORMIC ACID DECOMPOSITION

A cluster of papers reviewed at the Second Congress and also in the Elsevier Monograph (3) is concerned with the classic decomposition of formic acid at metal and oxide surfaces (5 to 8). For metal alloys, Schwab and his school (9) had indicated that the concentration of quasi-free electrons in the alloys was determinative of their activity. It was this work that led to wide acceptance of the "electronic factor" concept of catalysis, with Dowden (10), Eley (11) and their co-workers postulating an intermediate activated complex such as HCOOH^+ or HCOO^+ . Gold-palladium alloys whose d -band holes were regarded as the true catalytic agents suggested support for this view.

The electrical conductivity of nickel films on which formic acid vapor was

adsorbed, while initially conflicting in the results obtained (12, 13) tended, with the results of infrared adsorption spectra of adsorbed complexes, to indicate the presence of HCOO^- bands on copper, nickel, and zinc. On silver catalysts it was found that isotope effects with deuterated formic acids indicated reaction rates in decreasing order, $\text{HCOOH} > \text{HCOOD} > \text{DCOOH} > \text{DCOOD}$. While this suggested a nondissociative adsorption followed by a decomposition step, simultaneously releasing a hydrogen molecule, Otaki (14) by a study of the isotopic composition of the hydrogen $\text{H}_2\text{-HD-D}_2$, found that there could be no intramolecular decomposition.

The researches of Fahrenfort, Van Reyen & Sachtler (15) indicate that the rates of formation and decomposition of a formate on the metal catalyst surface best account for catalysis of formic acid decomposition on metals. On a noble metal such as gold, the adsorption step determines the rate of decomposition. With nickel, on the contrary, the adsorption step is rapid and the rate is determined by the decomposition of the surface formate. Experimental data suggest that the highest catalytic activities are found for metals of medium stability, Balandin's volcano curve (16), the most active surface being that which, under the reaction conditions, is about half-covered with the most stable adsorption complex.

Two reservations with respect to this general conclusion should be offered. It is dangerous, as Langmuir showed many years ago, to reason from the properties of a stoichiometric compound such as WO_3 to that of an adsorption complex of oxygen on tungsten, W-O . Secondly, as Schwab observed in discussions at Paris, a nickel formate containing some zinc formate had a stability vastly different from the pure nickel formate, which bears again on the "electronic factor" theory.

Finally in this matter, we should recall the work of Tamaru (17) on the simultaneous measurement of reaction rate and extent of formic acid adsorption during the progress of the reaction, using silver, copper, and nickel as catalyst surfaces. His data on silver and nickel conform well to the Dutch results. In the case of copper, however, the measurements of reaction rate and coverage appear only to be reconcilable if the reaction is occurring on merely a small fraction of the surface. The reaction is zero order at all observed reaction pressures, even though the adsorptions measured on the total surface increase with increasing reaction pressure. These observations point emphatically toward a restricted reaction as opposed to a reaction on a total surface. The results of Tamaru receive confirmation from results, reported by Smoluchowski at the September 1960 meeting of the American Chemical Society in New York, dealing with the properties of copper films, activated by radiation damage, in this same reaction of formic acid decomposition. Again, the fraction of the total surface which was active appeared minimal.

Eischens & Pliskin (5), using their infrared techniques on nickel and platinum supported on silica, conclude that adsorbed formate ion may not be the major chemisorbed species. They conclude also that the formate ion adsorption occurs on oxidized nickel rather than on the metal. There are variations in the spectra of adsorbed species with degree of coverage and with the

temperature of observation. They insist on the presence on the surface of what they term covalently chemisorbed formic acid, containing 17 electrons in the adsorbed resonance hybrid species, in contrast to the resonance hybrid of formate ion containing 18 electrons. The covalent form is said to be the less stable. The authors tend to discount the view of Sachtler (18) that the spectrokinetic data show the reaction to proceed via a formate ion intermediate. With platinum on silica as catalyst, the decomposition of small quantities of acid at -60°C . proceeds one-third by dehydration, the remainder as a dehydrogenation.

Infrared inspection of adsorbed formic acid on finely powdered nickel, on silica, and on alumina has also been reported by Hirota *et al.* (6). They find the acid adsorbed easily as formate ion on the metal, and probably as undissociated acid on the formate ion layer. Formate ion is found with alumina, but only in a physically adsorbed state from room temperature to reaction temperature on silica. These authors suggest a succession of consecutive steps in the decomposition mechanism but could not decide between several alternatives. With silica, dehydration is the primary step; with alumina, both a unimolecular mechanism and a consecutive mechanism via formate ions are indicated.

Using gold as catalytic material, Sachtler & de Boer (19) find that gaseous hydrogen molecules are not measurably chemisorbed below 200°C . When formic acid decomposes on a gold surface, hydrogen atoms partly cover the surface at the steady state. At 150°C ., these authors find no exchange between molecular hydrogen and deuterium, no formation of HD in formic acid-deuterium mixtures, equilibrium mixtures of H_2 , HD, and D_2 with mixtures of HCOOH and DCOOD or with HCOOD . The rates of the last two are characteristic of the reactions of the several formic acid decompositions. The authors conclude from these results that chemisorption of hydrogen atoms, not furnished by molecular hydrogen or deuterium but by any of the formic acid molecules, is essential for hydrogen exchange at 150° .

From a study of hydrogen oxidation on gold at 120° the reaction between molecular hydrogen and oxygen to form water is very slow. With formic acid and oxygen there is a fast formation of H_2O . With formic acid-oxygen mixtures in the presence of excess molecular deuterium there is fast formation of HOH containing only traces of HDO or DOD , and no hydrogen exists in the gas phase. The oxidation experiments are regarded as confirmatory of the conclusions reached from the exchange experiments at 150°C .

These results of formic acid decomposition on gold, in the opinion of H. A. Taylor (20), do not negate the Taylor-Thon mechanism. On the contrary, they are reconcilable with a mechanism put forward in the Reilly Lecture at Notre Dame in 1956 (21). The reaction sequence proposed was



Step 0 is the chemisorption, the center-making reaction. Step 1 with H(ads) struck by a molecule from the gas phase, is rate controlling. Step 2 is taken to be fast. The measured rate will depend on the number of centers, the chain length and the collision frequency. It is seen that 1 and 2 provide a chain mechanism. In the opinion of H. A. Taylor, these two reactions provide an explanation of the observations on the equilibrium isotopic molecules of H_2 , HD, and D_2 found by Sachtler & De Boer (19).

It would be decisive if there were some method of measuring chain lengths in these proposed chain mechanisms for surface reactions. Voevodsky, speaking in the Paris Congress for Semenov and himself on chain reactions at surfaces and alluding to the Taylor-Thon proposal, admitted that there was one clear-cut example of a chain mechanism induced at surfaces, an induced polymerization. This recalls the work of Parravano (22) who induced various polymerization processes in liquid systems with hydrogen electrolytically liberated at a palladium electrode, the hydrogen passing through the palladium membrane to induce polymerization in a solution of a monomer in contact with the outer surface of the membrane.

The decomposition of formic acid on silica gels and on glasses has been subjected to a comprehensive re-examination in an effort to determine the mechanism (8). Zero order surface reactions characterize all the surfaces examined. Also, the activation energies of dehydrogenation and dehydration are constant with all surfaces; only the selectivity or the activity changes. The selectivity is not related to the energies of activation nor is the activity proportional to the B.E.T. areas. They identify active centers on the surfaces with proposed topographical sites. If the number of surface OH groups exercises a considerable influence on the activity and selectivity of the surface the active centers have similar properties in certain conditions, causing the authors to consider the superficial surface of the solid as an entity related to the structure of the solid itself. In gels of varying pore size the authors conclude that the pores themselves are *not* the seat of the selective action as is sometimes suggested.

For a series of silica-alumina catalysts, Fisher & Sebba (23) examined activity for formic acid decomposition, choosing activation energy rather than specific reaction rate constant as the criterion of activity. They correlated the activation energies with the acidity of the catalyst as measured by *n*-butylamine titration. The pure alumina catalyst with the lowest titration value had the highest activation energy, 21.4 kcal./mole, the highest acidity catalysts showing activation energies in the neighborhood of 8.5 kcal./mole with a smooth curve between the extremes, for activation energy versus acidity.

RESEARCHES ON THE AMMONIA SYNTHESIS REACTION

It is fifty years since Haber's associates were providing the fundamental physico-chemical data on which the high-pressure synthesis of ammonia could be established. It was in early 1914 that the *Badische Anilin und Soda*

Fabrik were bringing the commercial process into operation. The mechanism of the synthesis process has been under constant research review for the last forty years. The results of such research, as of November 1959, were admirably summarized by Mars, Scholten & Zwietering in the Netherlands Congress (24). Slow chemisorption of nitrogen as the rate-determining step, the consequent kinetic relation derived by Temkin, and the doubts raised by Horiuti in his finding a stoichiometric number of the reaction $\nu_r = 2$ incompatible with the concept of slow chemisorption of nitrogen, led to a comprehensive re-examination of the problem by the Dutch workers. Owing to the strong dependence of the rate of chemisorption on the degree of coverage, methods had to be devised to measure this coverage under reaction conditions.

Chemisorption of nitrogen and the rate of ammonia synthesis on a singly-promoted iron catalyst were shown to be equal at the same temperature, nitrogen pressure, and surface coverage (25). The amount of nitrogen chemisorbed was measured gravimetrically. The nitrogen coverages calculated from the nitrogen fugacity P_{N_2} , and the chemisorption isotherm were in accordance with the coverages found gravimetrically. This work of the Dutch school supports the original thesis of Emmett and Brunauer (25a) that nitrogen ad- and de-sorption are the rate-determining steps in the synthesis and decomposition processes.

The Netherlands Congress report leads the Dutch school to the conclusion that the stoichiometric number is actually one, and they emphasize the necessity for extreme accuracy in the measurements in order not to get wrong results. Indeed, Horiuti believes that even the Dutch data do not unequivocally lead to a value of one. In an as yet unpublished report by Horiuti and Takezawa, the conclusion is reached that the value of one is in reality a lower limit to the possible value of the stoichiometric number. The Dutch authors also conclude that a clear understanding of the manner in which nitrogen is bound to the catalyst is still lacking. Indeed, the mode of binding may well be a function of the activity of the surface site. On very active samples, where synthesis can be measured even in the neighborhood of room temperatures, the nitrogen may dissociate at low coverages to form an immobile atomic adsorption. At higher coverages, in the range important for normal synthesis conditions, the nitrogen complexes may be partially dissociated molecules, e.g., $-N=N-$ or $=N-N=$, moving freely over the surface. The first hydrogenation step or its successor may be necessary to the complete dissociation of these complexes. From energetic considerations, the Dutch school conclude that the dihydrogenated surface complex has the lowest energy. With the whole system in equilibrium this would mean that the group, $Fe-NH_2$, will occur most frequently on the surface.

Ozaki, Taylor & Boudart (26), on the latter's suggestion, addressed themselves to these unsolved problems in the mechanism of ammonia synthesis by exploring the relative rates of ammonia synthesis with the two isotopes hydrogen and deuterium. They used two doubly-promoted iron catalysts in the

temperature range 218 to 302°C., at pressures from one-third to one atmosphere, and over a 300-fold range of efficiencies, i.e., the ratios of product yield to equilibrium yield under the given conditions. The surprising result emerged early that under identical conditions nitrogen-deuterium mixtures formed deuterioammonia more rapidly than did ammonia formation with hydrogen. To be precise, $-d(\text{cc. synthesis gas})/dt$ was fourfold larger with deuterium than with hydrogen at a given temperature, pressure, and space velocity. This result led to an initial reaction in favor of some mechanism involving both nitrogen and hydrogen as the slow step, as Horiuti had suggested. The massive evidence to the contrary (from Holland) gave pause to hasty conclusions. The experiments over the wide range of efficiencies, the kinetic behavior, pressure dependence, and isotope effect finally led to the conclusion that the rate-determining step is nitrogen adsorption, on a uniform surface or on a heterogeneous surface of the usual type, with, however, one added postulate, that the coverage of the surface consists principally of adsorbed NH in equilibrium with hydrogen and ammonia. If this view is correct the rate constant should be strictly proportional to the pressure, as found in the limited pressure range examined, whereas the Temkin equation demands a proportionality to $P^{1+\alpha}$ where α is the oftentimes variable exponent in the Temkin expression. The findings of Tamaru on the extensive adsorption of nitrogen and hydrogen on the surface during reaction are recorded in the succeeding paragraph. In order to reconcile his findings with the preceding review of the synthesis mechanism, it seems necessary to postulate that only a minor fraction of the total surface is active, a view that is supported by the extreme sensitivity of the synthesis process to traces of poisons such as water or water-producing gases in the synthesis mixture.

For forty years, measurements of the adsorption of reacting species and of products on catalytic surfaces have been made. Attempts to correlate the measured adsorptions of the single reactants with the kinetic data of the catalytic reaction have been consistently tried throughout this period, often with very fruitful results. It remained for Tamaru to make determinations of adsorption of the reaction species and products while the reaction was in progress (27). Reference has already been made to the significance of his measurements in the problem of the mechanism of formic acid decomposition on metal surfaces. At the Paris Congress Tamaru extended his studies to adsorption measurements during ammonia synthesis on a doubly-promoted iron catalyst. The results are especially striking and significant. Adsorptions during synthesis at 180° and 250°C. have been studied in a closed circulating system. Since ammonia was continuously removed from the system by traps, the rates always corresponded with the rate between nitrogen and hydrogen in the absence of negligible concentrations of ammonia. It was shown that (a) adsorption of nitrogen was considerably accelerated by the presence of hydrogen and that its rate of adsorption is almost ten times faster than the production of ammonia, (b) hydrogen adsorption during synthesis is not markedly affected by the simultaneous adsorption of nitrogen, and (c) adsorp-

tion was virtually unchanged when ammonia was removed from the ambient equilibrated mixture of nitrogen, hydrogen, and ammonia. The extensive adsorption of both nitrogen and hydrogen on the catalyst surface during reaction has to be reconciled with a variety of data on the synthesis process that have been accumulated during the last few years. We believe it seems necessary to postulate that only a minor fraction of the total surface capable of adsorbing the reactants is active in the synthesis process. Some of Tamaru's results point to the possibility that less than 0.2 per cent of the total surface may be active in the synthesis process.

Boudart (28) is examining the possibility that mobile adsorbates move over the surface to active sites where the synthesis is rapidly achieved.

The sensitivity of the chemisorption process with nitrogen to the state of the iron surface constitutes a still unsolved problem. The researches of Scholten (29) have decisively confirmed the earlier findings of McGeer (30) that the rate of nitrogen exchange reactions on reduced iron catalysts increases progressively with improved techniques of reduction of the iron catalyst. Scholten has now shown that, with extended reduction of iron synthetic ammonia catalysts, the temperature at which measurable chemisorption of molecular nitrogen and synthesis occur can be diminished from around 200°C. to room temperature. Extended reduction, with hydrogen introduced into the system through palladium membranes and for times of the order of 10^3 hr., is necessary to secure this result. These experimental facts, as yet, lack entirely any theoretical interpretation.

Mass spectrometer studies of the decomposition of ammonia in the presence of hydrogen on a series of metal films have been reported by Logan & Kemball (31). Activation energies and the pressure dependencies were studied on nickel, cobalt, rhodium, platinum, ruthenium, and rhenium, supplementing similar earlier work on iron. Nitrides are formed with vanadium and partially with tungsten and tantalum. The vanadium product is non-stoichiometric VN. Tantalum and palladium did not yield reliable measurements. Sintering occurs, which is drastic and is not complete even on films presintered in vacuo at 475°C. and continues during reaction. Six of the seven metals which gave reproducible results fall in Group VIII of the Periodic Table.

The kinetic data provide support for the view that the rate-determining step in the decomposition is the desorption of nitrogen with indices for ammonia and hydrogen in the ratio of 1 to -1.5 as required by the Temkin theory. The authors discuss their data in comparison with those of many others, as well as the relation of film data to bulk catalyst results. This discussion covers the important publications in this field for two decades.

Evidence for the chemisorption of molecular nitrogen on reduced powders from iron and cobalt oxides has been presented by Kokes (32). For iron, the amount chemisorbed at -195°C. corresponds to 10 to 20 per cent of a monolayer as determined by the B.E.T. method. For cobalt, the figure is between 50 and 60 per cent. These data recall earlier observations by Beeck (33), indi-

cating an initial heat of nitrogen chemisorption of 10 to 12 kcal./mole. The chemisorption is weak in all cases. It is unlikely that the nitrogen-nitrogen bond is broken in this type of chemisorption.

The monophosphides of vanadium, iron, manganese, and chromium are active in the decomposition of ammonia (34). Nickel, cobalt, and titanium monophosphides are inactive. Activation energies are lower with the phosphides than with the corresponding nitrides. Care was taken to exclude the possibility of interchange between nitrogen and phosphorus in the phosphide. No trace of phosphine in the exit gas was found. Changfoot & Sebba (34) thus suggest from this and earlier work with nitrides that intermediate formation of catalytic nitrides in ammonia synthesis and decomposition is unlikely.

RESEARCHES ON EVAPORATED FILMS

On evaporated films of the Group I_B metals, copper, silver, and gold, the surface potential difference brought about by the adsorption of hydrogen atoms has been examined by Pritchard & Tompkins (35). The atoms were produced by dissociation of hydrogen molecules on a hot tungsten cathode filament at 2100°C. There was no detectable adsorption of hydrogen at liquid oxygen temperatures by copper films when the filament was unheated. On six copper films, atomic hydrogen adsorption was rapid and complete and gave rise to maximum surface potential differences of -0.340 to -0.380 v., with an average value of -0.36 ± 0.02 v. The minimum amount of adsorbed hydrogen to give this potential change corresponds to a surface area of 180 cm^2 . A B.E.T. krypton adsorption gave surface area values of about 6000 cm^2 or, with uniform distribution of hydrogen atoms, a coverage of about 3 per cent. The authors suggest adsorption at the place of first collision followed by immobility and with the outer area, about 180 cm^2 , being substantially filled and producing the observed surface potential difference. The inner areas, when later covered, contribute insignificantly to the potential difference.

With silver and gold films, there was no adsorption of molecular hydrogen at -183° until the cathode filament produced atomization. With silver, the maximum potential difference at -183°C . had a mean value of -0.36 ± 0.01 v., and with gold -0.17 ± 0.01 v. In each case the adsorbed atoms appear to be immobile. The authors review all the adsorption data on these three metals and the previous conclusions. Conflicting results are noted. The authors believe that desorption of molecules sets in as soon as mobility occurs on the surface. They support the Bonhoeffer-Farkas mechanism for the *ortho*-*para* hydrogen conversion and suggest that the activation energy is that for surface diffusion of hydrogen adatoms. There is some evidence that there is another form of bonding of hydrogen atoms at higher temperatures.

An excellent and careful study of the mechanism of hydrogen exchange on evaporated platinum films has been reported by Boreskov & Vassilevitch (36). They studied, at 78° and 90°K ., the exchange reaction with molecular hydrogen isotopic gas mixtures and also the reaction between hydrogen ad-

sorbed on the platinum films and a molecular gas isotope. Both deuterium and tritium were used as well as protium. The velocity of exchange between adsorbed tritium and protium decreases rapidly with the extent of exchange. The authors attribute this to a heterogeneity of the surface. With feeble amounts of exchange the activation energy falls swiftly. On an important part of the surface the activation energy of exchange is expressible by a formula $E_{act} = 5.2 \pm 2.1S$ kcal./mole, where S is the extent of exchange per cent. The velocity is independent of the hydrogen pressure. Substitution of deuterium for protium in the gas phase does not alter the rate of exchange with adsorbed tritium. Substitution of protium for tritium as the adsorbed phase increases the rate of exchange with gas-phase deuterium in the ratio 7:1. Comparing the kinetic isotopic effect with the separation factors, measured with tritium and protium and calculated thence for deuterium, the authors conclude that the number of atoms of adsorbed hydrogen that pass into the gas phase when the activated complex breaks up (called by them the molality M of the reaction) is unity. A Bonhoeffer-Farkas mechanism would call for $M=2$ and, as these authors find, zero reaction order. Two Eley-Rideal mechanisms discussed by Schuit (37) would both call for $M=1$ but the orders of reaction would be either 1 or $\frac{1}{2}$ to 1. Boreskov and Vassilevitch therefore propose a mechanism of exchange with pre-adsorbed isotope in which an adsorbed atom liberates itself from the surface to form a hydrogen molecule (or perhaps a positive ion molecule H_2^+) bound to the surface, with an activation energy of 5 to 7 kcal./mole. The molecule formed remains fairly strongly bound to the greater part of the surface and its transfer to the surrounding volume demands a considerable activation energy. The authors assume an easy displacement of one of its atoms to a neighboring adsorbed atom of hydrogen. This diffusion over the surface would occur more easily than the first stage of formation of the adsorbed molecule (ion). The authors have shown that a part of the surface is characterized by a low energy of activation of exchange and hydrogen adsorbed on these areas rapidly equilibrates with the gaseous phase. Vacant sites thus formed receive atoms from the gas phase. An adsorbed atom of tritium is thus replaced by an atom of protium giving the value $M=1$, as found.

Isotopic exchange between isotopic molecules in the gas phase at 78°–90°K. occurs without participation by the greater part of the adsorbed hydrogen discussed in the preceding paragraph. The molecular exchange occurs on a small fraction of the total surface, the order of reaction is 0.5 and the activation energy 1.2 kcal./mole. The pre-exponential factor is low, of the order of 10^{-4} to 10^{-5} . The reaction times are measured in minutes, whereas the exchange with adsorbed tritium consumes hours. The authors give a modified Rideal-Eley mechanism II for their interpretation of this molecular exchange, which above 300°K. goes over to an unequivocal Bonhoeffer-Farkas mechanism by reason of the rapidity of the desorption process.

Schwab (38), reporting on a thesis of Killman (Munchen, 1959), for the exchange reaction of H_2 - D_2 mixtures on nickel foil at temperatures between

100 and 165°C. with apparent activation energies of 7.5 kcal./mole, rejects both the Bonhoeffer-Farkas and Rideal-Eley mechanisms and suggests one that is termed a Langmuir-Hinshelwood mechanism, interaction between adsorbed molecules. In parenthesis, Schwab writes (atom-pairs) for these molecules. These adsorbed molecules are expected to interact with lower activation energies than adsorbed atoms.

Exchange between deuterium and pre-adsorbed hydrogen on evaporated nickel films, supported nickel catalysts, tungsten films, and tungsten powders was also reported on by Gundry (39). The pre-adsorbed isotope always appeared in the gas phase as an equilibrium mixture of H_2 , HD, and D_2 . In all cases studied the surface was *heterogeneous*, only a few per cent at most being in equilibrium with the ambient gas at liquid air temperatures. The adsorbate is adjudged immobile. At higher temperatures, greater fractions of the surface become active. With tungsten, it is estimated that even at 373°K. some 10 per cent of the surface is still inactive. Mercury vapor inhibited all activity, but a more surprising inhibitor was molecular nitrogen which apparently forms a monolayer on a nickel film at 78°K. Desorption of this nitrogen occurs readily at room temperature with restoration of the 78°K. activity. The adsorption of nitrogen is assumed to be in an undissociated form with a heat falling from 10 kcal. to 3 kcal./mole at high coverage. Nitrogen is apparently adsorbed even on top of adsorbed hydrogen once the hydrogen coverage is significant. Hydrogen displaces pre-adsorbed nitrogen from the surface. Oxygen, which is more strongly adsorbed than hydrogen, is not an effective poison in quantities less than a monolayer.

The low temperature interaction of oxygen with evaporated germanium films has furnished to Bennett & Tompkins (40) an intimate picture of the adsorption process and the succeeding incorporation process into the germanium lattice. The temperature range studied was from 78 to 493°K. At all temperatures an initial fast process followed by a slow uptake occurs; this is dependent on the square root of the oxygen pressure and following an Elovich rate equation. Sorption was mainly irreversible with perhaps a 0.1 per cent coverage less strongly held, probably molecular oxygen. The fast uptake varied from 0.3 at 78°K. to 1.0 atom per site at 273°K.; after the slow uptake, 2 to 3 atoms per site were taken up between 273° and 493°K. At 78° and 90°K. a reversible molecular physical adsorption with an isosteric heat of 3 kcal./mole is noted. Incorporation of oxygen into the lattice occurs at all temperatures. The activation energy increases with increased incorporation, with values ranging from 1.56 kcal./mole with 0.64 sites occupied, to 6.33 kcal./mole when the oxygen uptake was 1.87 atoms per site. Initial rapid adsorption and incorporation produce considerable loss of area that, in this particular case, can be well defined as to the extent of sintering. It may also occur with other films undergoing rapid exothermic adsorption processes. The mechanism of the oxygen uptake has been interpreted in terms of place-exchange not over the whole surface but probably at terminations of dislocations at the surface, at kink sites, or at terraces, the number of these being very small compared with the total number of adsorption sites.

The adsorption of iodine on evaporated films of tungsten has now been compared with the adsorption of hydrogen on such films (41). Measurements were made between 0° and 300°C., the low temperature measurements permitting comparison with W/H_2 at 0°C. The hydrogen measurements indicate that sintering at 150° and 300°C. had less effect than might have been expected, reducing the capacity of the surface to adsorb hydrogen at 0°C. by 11 and 31 per cent respectively.

The results with iodine indicate that dissociative adsorption occurs on the glass walls of the containing vessel, in increasing degree with baking of the glass. On admission of iodine to the tungsten films the initial doses were taken up instantaneously at 0° or 150°C. Later doses and all doses at 300°C. were only partially adsorbed, leaving a residual pressure decreasing with time. Attempts to desorb the iodine by reducing the pressure were unsuccessful. It appears from the results that the coverage with iodine corresponds to a monolayer approximately 50 per cent of that yielded by hydrogen. From the radii of tungsten, iodine atoms, and ions it is suggested that iodine atoms can only occupy alternate sites on the surface and this limits the observed coverage. The initial heat of adsorption of iodine atoms is about 70 kcal./mole; the formation of iodide ions on the surface is probably endothermic to the extent of 10 kcal./mole. There is evidence also for a phase change in the surface with a value of -4.5 kcal./mole for the change in heat content on formation of the complex.

Field emission studies of the adsorption of iodine on tungsten were performed to supplement the low temperature adsorption work (42). Iodine is desorbed from the tungsten emitter at temperatures above 1500°K. The field emission patterns are identified in terms of the different crystallographic planes on the emitter with evidence that the "triangular" sites which occur on the [111] planes are favorable for iodine adsorption.

Krypton forms a monolayer on iron films at 78°K. at pressures of 0.02 mm. (43). The isotherms obey the B.E.T. equation even though the relative pressure range is abnormal. Hence, the adsorption can be used for studying the pre-treatment of the surfaces. Sintering occurs with an activation energy of 4 kcal./mole at 23°C. and pressures less than 10^{-6} mm. with films prepared at 78°K. Vacancy cluster diffusion is proposed as the mechanism. In the presence of oxygen there is some "incorporation" in the film even at 78°K., preceded by a fast exothermic chemisorption that produces sintering of the film, leading to a decrease in the area available to krypton adsorption from one-third to one-sixth of the initial film area. There is no similar effect with fast hydrogen chemisorption. This resulted in a small increase in the volume of krypton adsorbed. The adsorption of hydrogen also manifestly stabilized the film against sintering at 23°C. Roberts discusses the energy of interaction of inert gases with surfaces and the influence of chemisorbed gases in the light of the equation derived by Singleton & Halsey (44), the Kirkwood-Muller dispersion force theory (45, 45a), that of Ehrlich & Hudda (46) in terms of polarization forces, and in terms of the charge-transfer theory of Matsen, Makrides & Hackerman (47). With respect to this latter theory,

Gundry & Tompkins conclude (48) that this latter charge-transfer no-bond theory may possibly be replaced by one involving polarization energy.

With reference to krypton adsorption as a means of B.E.T. determinations, Gaines & Cannon (49) conclude that fairly complete monolayers of gases such as krypton should be formed before multi-layer formation becomes significant. On the basis of their examination of the adsorption energetics and their own experimental data the authors conclude that recent criticisms of the use of krypton for surface area measurements are not justified.

An unexpected reaction path was disclosed by Moss & Kemball (50) in the catalytic decomposition of cyclohexylamine in presence of excess hydrogen on evaporated platinum films, in the range of 100–150°C. The initial products are ammonia, benzene, and a little cyclohexane. The benzene was hydrogenated to cyclohexane only after most of the amine had been destroyed. Examination of the behavior of aniline under similar conditions, and the hydrogenation, exchange, and deuteration of benzene in the presence of cyclohexylamine were studied. The authors conclude that, before decomposition, the cyclohexylamine dissociates to form an adsorbed species equivalent to adsorbed aniline. The rate-determining step of the decomposition is the breaking of the C—N bond ($E = 18$ kcal./mole). This yields a nitrogen-containing species that is immediately desorbed as ammonia, leaving a phenyl radical that is then converted to benzene. Cyclohexylamine is a poison for the hydrogenation of benzene by a factor of 10^4 . Exchange of benzene is also inhibited. Since this reaction occurs in the range 45–100°C., the adsorption-desorption of benzene must be a rapid process above 100°C. even in presence of cyclohexylamine. The exchange reaction indicates both phenyl and phenylene radicals on the surface.

REACTIONS ON DUAL COMPONENT CATALYSTS

It appears certain that platinum can be dispersed on suitable supports in approximately atomic dispersion (51). Hydrogen adsorption is a useful and reliable tool to study the dispersion of the metal on oxide supports. The extremely high dispersion ($<10\text{\AA}$) of platinum on alumina was demonstrated. With metal crystal sizes larger than 50Å but smaller than 1000Å, hydrogen chemisorption gives values identical with those obtained by x-ray line broadening. With unsupported platinum of crystal size larger than 1000Å, the hydrogen chemisorption and B.E.T. nitrogen adsorption give practically the same specific surface area.

Weisz (52) addresses himself to a discussion of catalysis by geometrically separate and different catalytic components that each catalyse separate steps, the chemical intermediate existing as a true compound but of indefinite concentration. He defines as a non-trivial polystep reaction, $A \rightarrow B \rightarrow C$, one in which the conversion ϵ_{AC} is very much greater than the product of the conversions $\epsilon_{AB} \times \epsilon_{BC}$. Having discussed the mass transport criteria involved, he considers a number of hydrocarbon reactions, paraffin isomerization, hydro-

cracking, and aromatization of C_4 -cyclics. He also discusses interception of intermediates and catalyst selectivity in terms of a catalyst X operative in the two steps of the sequence $A \rightarrow B \rightarrow C$ and a catalyst Y that can deflect B to a product D. He shows that an α methyl cyclopentane dehydrogenative system on platinum-silica catalysts, leading to methyl cyclopentadiene, is intercepted by the introduction of acidic catalyst centers to produce 6-membered rings. In hydrogenative conditions, the second steps may produce paraffinic cracked products or 6-membered C-rings. On such a dual-component catalyst, progressive deactivation of the platinum by hydrogen sulfide first causes a decrease in hydrogenolysis products and an increase in C_6 -rings. Further poisoning finally kills all activity by removing the generating step for both product paths.

In addition to the two consecutive reactions discussed by Weisz (52), de Boer & Van Der Borg (53) also discuss the variations that are introduced by a direct conversion of A to C, requiring thereby a third rate constant. The conditions required to promote selectivity are comprehensively analyzed. Factors that promote selectivity, where B is the desired product, include higher reaction temperatures, less active catalysts, and a lower concentration of hydrogen if the reaction involves hydrogenation. The literature reveals that these three factors are of importance in the hydrogenation of oils to form oleic acid and preferably not stearic acid. Selectivities varying from 0.7 to 25 can be secured with 10 per cent platinum on carbon or 2 per cent nickel on kieselguhr, using these three variables; platinum, being the more active of the two catalysts, shows lower selectivity. With the nickel catalyst, changing the hydrogen pressure at 180°C. from 1 to 100 atm. decreased the selectivity from 25 to 2. It is also known from the literature, paralleling Weisz's observation on poisons in the preceding paragraph, that a sulfur-poisoned nickel catalyst may suppress the hydrogenation of oleic ester completely.

From a study of the kinetics of *n*-pentane isomerization over a platinum-alumina catalyst at 372°C. (54), in a flow reactor using hydrogen at pressures ranging from 7.7 to 27.7 atm., and hydrogen to *n*-pentane ratios ranging from 1.4 to 18, the rate of isomerization has been found to correlate with the *n*-pentane to hydrogen mole ratio and to be independent of the total reactor pressure at a fixed hydrocarbon-hydrogen ratio. The results obtained can be explained in terms of a mechanism whereby isomerization proceeds via an olefin intermediate present in equilibrium concentration. The mechanism assumes that *n*-pentane dehydrogenates on platinum sites to *n*-pentene, which in turn migrates to acidic sites to isomerize, presumably by a carbonium ion mechanism. Under the conditions studied, the rate-controlling step is the isomerization of the intermediate olefin on acidic sites.

In a succeeding paper from the same senior author (55) the kinetics of methyl cyclohexane dehydrogenation were investigated between 315° and 372°C. at partial pressures from 0.7 to 2.2 atm. in the presence of hydrogen from 1.1 to 4.1 atm. The reaction was found to be near zero order with re-

spect to both hydrocarbon and hydrogen over the range studied. This suggests that the active sites are heavily covered with adsorbed molecules or radicals under reaction conditions. The activation energy for the reaction was found to be 33 kcal./mole, and a kinetic scheme given suggests that the reaction rate corresponds to the rate of desorption of toluene.

The powerful adjunct to catalytic research, made available by the gas chromatographic analysis apparatus developed initially by Kokes, Tobin & Emmett (56), is well illustrated by a paper from the Dutch Shell Research Laboratories (57) last year. A micro-reactor was coupled with the gas-chromatographic analysis apparatus to determine the reactivities of thirty individual C_6-C_8 naphthenes over platinum-alumina halogen catalysts at 350°C. The microtechniques employed permitted this study with the excellent pure hydrocarbon samples generally only available in small amounts, supplied by the American Petroleum Institute. The reactions were conducted at atmospheric pressure using excess hydrogen. Cyclopentanes and 1,1-dimethyl cyclohexane are converted to aromatics much more slowly than are ordinary cyclohexanes. The data with the cyclopentanes again suggest, firstly, dehydrogenation to olefines that then migrate to the acidic sites, forming carbonium ions. Skeletal isomerization of the ions to form cyclohexyl structures is taken to be the slow step in the reactions leading to aromatics. Relative rates of alternative paths are given by simple ratios for relative carbonium ion stabilities multiplied by the number of possible paths. With two adjustable parameters the data for 21 cyclopentanes can be fitted.

Extending an earlier-developed technique with hydrocarbons (58), Galwey & Kemball have used catalytic exchange with deuterium to study the breakdown of molecules adsorbed on a nickel-silica type developed by Schuit of the Shell Laboratories in Amsterdam (59). The new studies are concerned with simple alkyl halides and oxygen-containing compounds such as simple alcohols, ethers, and ketones. The alkyl halides like the hydrocarbons are dissociated on the metal to form species that are stable over a temperature range of 20° to 200°C. The oxygen-containing compounds appear to be adsorbed mainly on the silica support at 0°C. and very little dissociative adsorption occurs on the nickel at this temperature. With the alkyl halides there is a rapid exchange of a limited number of hydrogen atoms at 0°C. after adsorption has been allowed to occur at any temperature between 0° and 200°C. Adsorbed alkyl radicals and alkene molecules are important intermediates. With cyclohexene two hydrogen atoms rapidly exchange at 0°C. after adsorption in the range 0°-180°C., indicating a stable species C_6H_8 . Dissociation of the hydroxyl hydrogen atom, pre-adsorbed on the silica, occurs on the nickel at 20°C. With the ethers, the main adsorption is on the support and the unambiguous interpretation of the results is impossible.

Three theories for calculation of the initial distribution of products from the exchange of deuterium and propane have been considered by Kemball & Woodward (60). In this paper they criticize interpretations put forward by Addy & Bond (61) concerning their work with iridium, palladium, rhodium,

and platinum. The main mechanism of the exchange reactions on metal films, it is concluded, is by interconversion of adsorbed propyl radicals and adsorbed propylene molecules; but triply-attached species, formed by dissociation of one hydrogen atom from each carbon, may also take part in the reaction.

Ruthenium, when used with palladium or platinum, displays a synergistic effect in various catalytic reductions (62). Use of the single catalysts in several reactions failed, or the rates were slower. A mixture of two, one of which was ruthenium, was often successful. A succession of stages in the over-all process is one possible explanation.

With palladium on alumina, Hamilton & Burwell (63) find that 2-butyne and hydrogen reach a steady state with respect to selectivity and stereospecificity rather slowly but much more rapidly than a constant rate of reaction.

A zinc catalyst, prepared by extraction of aluminum with sodium hydroxide from a 1:1 Zn-Al alloy until only 3 per cent of the aluminum remains (64) when transferred moist to various hydrogenation systems, reveals the following: Zinc does not cause the hydrogenation of olefins. It catalyses the selective hydrogenation of acetylenic to ethylenic compounds. It accelerates the reduction of aldehydic and ketonic C=O groups.

Supplementing the earlier work of Eischens & Pliskin (65), Little, Sheppard & Yates (66) have discussed in a new publication the infrared spectra of chemisorbed acetylene and ethylene on silica-supported metals. Combining the two sets of results leads to a picture in which the information obtained is an approximate value of the ratio of CH_2 to CH_3 groups after hydrogenation of the two chemisorbed hydrocarbons on the surface. The ratio is three for ethylene on both nickel and palladium, three for acetylene on nickel, and at least five for acetylene on copper and palladium, with a possible error of ± 1 . The data show that, if the surface species are predominantly *n*-alkyl groups, a limited amount of polymerization has occurred on the surface. This is most extensive with copper and palladium.

For the initially adsorbed hydrocarbons there is greater variation. Both olefinic and saturated species are formed with ethylene on each metal; the proportion of olefinic groups is greater for palladium than for nickel. With acetylene, Little, Sheppard & Yates obtained only olefinic species on palladium and copper but Eischens & Pliskin report only saturated species with nickel.

Using all the resources of modern catalytic research including mass spectrography, gas chromatography, and 1-C^{14} labelled *n*-octane, Pines & Chen (67) once more have studied the mechanism of catalytic aromatization of paraffinic hydrocarbons. Since the catalytic properties of aluminas depend on their mode of preparation, aromatization has been studied with chromia alone and with chromia-aluminas A and B, in which the former (A) had intrinsic acidity and the latter (B) had very weak intrinsic acidity. Reactions were conducted at atmospheric pressure and 500°C . It emerged immediately that distribution of products varied markedly with the extent to which the

reaction had poisoned the catalyst during use, and that the modes of production of aromatics varied with the three types of catalyst used. Five-, six-, seven-, and eight-membered ring intermediates can be involved in the process to extents varying with the catalysts. The C^{14} distribution indicates that larger ring intermediates are formed on the less acidic alumina supports while cyclopentanes can result from the more acidic catalysts. The arrangement of the chromia on the surface is also important in directing specific ring closures. The conclusion seems inescapable that the catalysts have a variety of active sites that can be deactivated to different degrees during the aromatization reaction.

Even after drying at 1000° , γ -alumina continues to evolve traces of water on further heating. This bound water on the surface is known to affect the catalytic properties. Infrared studies of transparent sheets of alumina aerogel (68) reveal initially both hydroxyl groups and water molecules. At 400°C . these latter have disappeared, but many hydroxyl groups remain. Heated above 650°C ., alumina still shows three bands assignable to "isolated" hydroxyl groups that may be eliminated by further heating or revealed by exchange with deuterium, but the groups are removed at unequal rates. The surface coverage by hydroxyl groups after drying at 400° is estimated to be 40 per cent and only 2 per cent after drying at 800°C . It is suggested, but not proved, that the attachment of hydroxyl groups is ionic in character. There are differences in the "acidic" character of the three groups remaining at 650° , as revealed by the infrared studies and measured by their ease of exchange of hydrogen.

Using infrared techniques, Peri (69) has examined the adsorption and isomerization of butene on gamma-alumina aerogels in plate forms. Strongly adsorbed butene on alumina below 4 per cent coverage is olefinic in character and resembles *cis*-2-butene in spectral appearance. No evidence was found for adsorbed radicals or organic ions. Active sites for strong adsorption and isomerization appear to be Lewis acids.

An irreversible exothermic transformation of silica-alumina gels occurs about 580°C ., according to Prettre and his co-workers (70). At this temperature a maximum of protonic and Lewis acidity, a slowing up in the loss of weight, and a marked diminution in the adsorption of ammonia are noted. Water vapor lowers the temperature at which these phenomena are produced. The exothermic reaction has a strong influence on the catalytic activity. The presence of soda suppresses the exothermic reaction. Removal of the sodium by acid exchange yields a gel which then undergoes the exothermic change.

HYDROGEN ADSORPTION AND DESORPTION FROM SURFACES

Of the first six communications to Section 1 of the 2nd International Congress, five were concerned with the adsorption of hydrogen on evaporated nickel films (71, 72), on platinum black at low temperatures (73), on molybdenum silicide (74), and on zinc oxide (75). We select the novel communication by Sandler (74) from these.

Materials such as MoSi_2 and VS_2 can be prepared by an arc-melting technique from stoichiometric quantities of the elements. They can be shown by x-rays to be single phase materials. They are brittle and can be ground to fine powders. They have a high metallic conductivity of the same order of magnitude as the corresponding metals. That they have catalytic properties similar to those of the transition metals has been established by Sandler using adsorption of hydrogen, hydrogen-deuterium exchange, and the parahydrogen conversion as criteria. There is a high activity for the exchange at 77°K. and a fast parahydrogen conversion, partly magnetic in origin. This indicates that a large fraction of the molybdenum surface ions is exposed and that these ions are paramagnetic. There are different types of hydrogen adsorption; one a high-temperature-activated adsorption which poisons a reaction that occurs on sites at low temperatures. The exchange reaction has different positive temperature coefficients in two distinct areas, below 200°K. and above room temperature. These regions are separated by a region with negative temperature coefficient, attributable to poisoning of the sites for the low temperature exchange by the high temperature adsorption. This negative temperature range does not correspond to a stable adsorption state. The data obtained recall the Kummer & Emmett data (76) on a singly promoted iron catalyst, which suggested to Emmett a Type C adsorption.

The nature of the topography of hydrogen adsorbed on a tungsten crystal tip was discussed by Sachtler & Dorgelo at the 4th International Congress of Electronic Microscopy in 1958, a reprint of which has appeared this year (77). Field emission patterns taken during hydrogen desorption from the tungsten tip not only show the existence of a positive hydrogen species on the surface but indicate a progressive removal of the positive hydrogen, first from the [100] regions; whereas, the [111] regions retain their gas quite tenaciously and only release them after extended heating. This is confirmed in the initial stages of adsorption onto clean tips, the [111] areas immediately becoming bright (positive), the [100] areas remaining invisible until additional time has elapsed. The authors link "adsorption" with "crystal growth from metal vapors," and justify this by stating that the bonding forces in chemisorption on metals are of a similar nature to bonding forces in the metal crystal. The topographical explanation for the two types of binding of hydrogen is associated by Sachtler and Dorgelo with the atom arrangements of the [100] and [111] faces of a face-centered cubic lattice. A-sites are situated between four metal atoms in the [100] faces. With [111] faces there is room for both A-sites and B-sites, each site between three metal atoms, and each A-atom surrounded by three B-atoms and vice versa. A-sites adsorb atoms with small negative charge. It is on the B-sites that the positive charge of the second hydrogen species is located. The heat of adsorption of the latter should be intermediate between that on A-sites and physical adsorption. Desorption or dilution of adsorption gives an opportunity for a B-site adsorbate to move over towards an A-site. The second species of adsorption will occur preferentially on [111] rather than [100] faces. This topographical interpretation can be correlated with earlier work on the changes of resistance

of nickel films that occur with increased hydrogen adsorption (78). It is also in agreement with kinetic data on hydrogen adsorption, in particular with that of Gundry & Tompkins (79) that calls for an initial state, C_i , and a firm adsorption state, C_f , the hydrogen molecule being unable to pass directly from the gaseous to the firm state of adsorption.

Using an ion gauge and a field emission electron microscope, Becker (80) has summarized his observations on hydrogen adsorption on single crystal surfaces of tungsten. From the ion gauge data one can determine the rate of adsorption, and the amounts adsorbed as a function of time, pressure, and tungsten surface temperature. The emission microscope reveals how the electron work function changes with the several variables. On most planes the work function increases linearly with increased coverage until there is an H adatom for every two W surface sites. Then, the work function increases more rapidly until the ratio H to W is unity. As many as five adsorption "stages" are recognizable. The number of H adatoms and the change in work function per stage vary considerably for different planes. The sticking probability is about 0.27 in the earlier stages (1 and 2) of chemisorption of hydrogen. For stages 3 and 4 it is appreciably less and is very small for stages 5 and higher.

At temperatures in the range of 1200° to 1800°K., and at pressures in the range 10^{-2} to 10^{-6} mm., the old problem of dissociation of hydrogen on filaments of platinum and gold and of oxygen on filaments of platinum has been restudied. The atomization of hydrogen on carbon filaments made by carbonization of wood-pulp cellulose has also been studied in the temperature range 1700° to 2000°K. (81). Molybdenum oxide proved to be an effective trap for the hydrogen atoms emitted, and a reduced form of the oxide was an equally efficient trap for oxygen atoms, reacting only slowly with molecular oxygen. The rate of atomization is proportional to \sqrt{P} at lower and to P at higher temperatures. In the systems H_2/W , H_2/Pt , H_2/Au , and O_2/Pt the kinetic data justify a mechanism of adsorption to yield a state M-G, of mobile nature, from the diatomic gas G_2 , followed by an evaporation of the gas atom. The rates are those that would be expected from reaction in an isothermal box. The atoms and molecules evaporate in their equilibrium ratio, and sticking coefficients can be deduced.

With carbon filaments the reaction was accurately first order, with a low sticking coefficient of 6×10^{-4} at 2000°K., indicating again a layer of adsorbed atoms with free translation over the surface. The adsorption of molecular hydrogen on carbon requires an activation energy, as high as 56.3 kcal./mole, considerably higher than those obtained earlier from adsorption studies on amorphous carbons (which seemed to reach a limit of 30 kcal./mole) but sensitive to the degree of graphitization (82, 83).

CONCLUSION

In conclusion, I append a few paragraphs from my concluding remarks at the Paris Congress, July 1960, that summarize my own development over

the years in the problem of surface catalysis and extends to others the opportunity for fruitful further work in this field.

Thirty-five years ago in examining the problem of "active centers" in catalytic reaction, the suggestion of varying activities of plane faces, corners, edges and even extra-lattice atoms of catalyst surfaces was proposed. More conservatively, and with less commitment, some six years later, in developing the concept of activation energy of adsorption, it was emphasized that, where a desorption process was rate-determining, the "active center" would be that area of the surface where the activation energy of desorption, the sum of the activation energy of adsorption, E , plus the heat of adsorption, Q , showed a minimum in the curve of $E+Q$.

At the First International Conference in Philadelphia, Tamaru & Boudart (84) provided an excellent example of a desorption rate-determining process in the decomposition of germane on a germanium surface. The surface was shown to be reasonably uniform and essentially covered with a monolayer of adsorbed hydrogen atoms. The order of reaction was zero and the reaction was thus identified as a desorption of hydrogen molecules from the monolayer.

In continuation of this work Dr. Joseph Kuriacose, desiring to determine the characteristics of the germanium film laid down, prior to a study of doped films, introduced two platinum electrodes into the glass reaction vessel which would permit determination of the electrical resistance of the built-up germanium film. An entirely unexpected result emerged from these experiments.

Dr. Kuriacose (85) confirmed quantitatively the rate of decomposition of germane in empty glass vessels as found by Tamaru. When, however, the conditions were modified by the introduction of two platinum contacts, spaced some 12 centimetres apart, the velocity of decomposition of the germane in the reaction vessel *increased four-fold!* (It is to be understood that there was no applied potential between the contacts during the reaction.) The increased reaction was not occurring on the platinum. A platinum wire heated to reaction temperature in a cold glass vessel did, indeed, decompose germane rapidly for the time required to lay down a cover of germanium on the platinum, after which the rate fell steeply to that which would be characteristic of the small surface area of germanium thus produced. The increased rate of reaction appears therefore to be due to two small areas of contact between germanium and the platinum metal. It was established that, in spite of the observed acceleration, both the zero order of reaction and its apparent activation energy remained unchanged.

In the contact between the metal and the semiconductor there is produced a barrier layer with rectifying properties extending into the barrier layer to a distance of the order of magnitude of 10^{-8} cm. or less. It is in this area that we locate the cause of the observed acceleration. We conclude that, because the kinetics of the process has not been changed by the active area, the mechanism of the reaction remains, as in absence of the areas, the decomposition of germane over the whole germanium film. It has been shown in this latter case that desorption of hydrogen is the rate-determining step. Hence, the contact area appears to accelerate this step. We conclude therefore that, since the mechanism is the same in the two cases, normal and accelerated, the activated surface diffusion of hydrogen atoms over the germanium surface appears to be the slow step. The earlier experiments of Tamaru and Boudart on the adsorption of hydrogen on germanium films, where the Langmuir isotherm was obeyed at low coverage, $\theta = bp^{1/2}$, pointing to dissociative adsorption. A statistical-mechanical calculation of the pre-exponential part of b showed the adsorption to be of the immobile type.

We see an interpretation of the results obtained in an activated diffusion of hydrogen atoms over the surface to an active area at the metal contact which collects hydrogen atoms from a zone surrounding it, thereby speeding up the reaction rate, becoming a "porthole" for the desorption act.

This view recalls much earlier work relative to the activity of interfaces between two solid phases and especially those examples which led Schwab, in 1929, to a formulation of the "Adlineation Theory" (85). The striking effect observed with the platinum-germanium contact is offered as a clear-cut example of adlineation. It opens up new possibilities for further exploration. One obvious line of research involves the study of velocity and extent of adsorption of hydrogen at metal centers on, for example, silica or silica-alumina supports as contrasted with the rate of adsorption in the absence of the metallic "porthole." We believe that the concept has important consequences of theoretical and practical significance.

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NUCLEAR AND ELECTRON SPIN RESONANCE^{1,2}

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This review is restricted to the chemical application of nuclear and electronic magnetic resonance. Cross relaxation, Maser action, most of the work on dynamic polarization, and use of the Mössbauer effect for observing magnetic resonance will not be classified as chemical. The discussion will be divided into sections on the magnetic resonance of electronically diamagnetic and paramagnetic materials respectively. The former contains nuclear resonance (NMR) almost exclusively, while the latter includes both nuclear and electronic resonance (ESR).

HIGH RESOLUTION SPECTROSCOPY OF DIAMAGNETIC MOLECULES

As the available instruments improve and the factors governing attainable resolution come under better control, the quality of spectra appearing in the literature improves correspondingly. The depth of interpretation of high resolution spectra has ranged from empirical assignment of chemical shifts and spin-spin coupling constants, to attempts to calculate all the details of the spectrum of a molecule from sufficiently accurate wave functions.

The positions and intensities of all the lines in NMR spectra are most conveniently summarized by numerical parameters in phenomenological or spin Hamiltonians. The parameters are, in addition to the magnetic moments of the nuclei, chemical shift constants for each of the nuclei and spin-spin coupling constants for each pair of nuclei. With appropriate isotopic substitutions it is usually possible to obtain the constants in the spin Hamiltonian from the spectra, but the process is laborious for complicated molecules.

Corio (1) has given a carefully worked out review of methods for determining the parameters in the spin Hamiltonian from the spectrum. He makes full use of symmetry and conservation properties. While the methods may seem too abstract to many who work in NMR, they are essential for an economical solution of the problems that arise.

As examples of complete determination of the parameters in spin Hamiltonians, we may cite work on ethyl acetylene (2, 3) and ethyl mercaptan (2), ethyl derivatives of mercury, silicon, zinc, and germanium (4, 5) substituted ethylenes (6), propenes (7, 8), butenes (9), and vinyl compounds (10).

The spectrum of propane has been analyzed by an elegant theoretical method (11) that takes full advantage of the molecular symmetry, and by

¹ The survey of literature pertaining to this review was concluded on December 15, 1960.

² The following abbreviations will be used: NMR, nuclear magnetic resonance; ESR, electron spin resonance.

examination of the satellites associated with C^{13} -H splitting from the natural abundance of C^{13} (12). Results of the two methods are in agreement. Thorough analyses that include illuminating theoretical or computational methods have been made of epoxides (13), fluorobenzene (14), crotonic acid derivatives (15), dimethyl formamides (16), and deuterated aromatic compounds (17).

The correlations between structure and magnetic resonance parameters, established by investigations of substances whose structures are well known, have been used extensively to determine some features of structure in complex molecules and the effects of environment on structure. Conclusions have been reached concerning structures and conformations of nucleosides and nucleotides (18, 19), resin acids (20), vinyl esters (21), indoles (22), and boron-nitrogen compounds (23, 24).

ORIGIN OF CHEMICAL SHIFTS AND SPIN COUPLINGS

The investigations of chemical shifts and spin couplings have blended theoretical work and experimental observations in all proportions. Calculations have been made for the contributions to shielding of protons by: electric fields (25), Van der Waals interactions with solvent molecules and bond formation (26, 27), and solvent molecules through their magnetic anisotropy (28). Interactions with the solvent frequently produce different chemical shifts at different positions in a molecule and sometimes it is possible to produce changes in spectra that facilitate interpretation (29, 30, 31).

Studies of $C_6H_5^-$, C_6H_6 , and $C_7H_7^+$ (32), and of methyl substituted naphthalenes (33) suggest a contribution to proton shielding in aromatic systems proportional to the π -charge density on adjacent carbon atoms. The proton shielding in cyclo-octatetraene and its dinegative ion are identical despite the difference in charge densities. Katz (34) has argued that the dinegative ion is planar, the neutral molecule non-planar, and the increased shielding associated with the increased charge density in the ion is just of compensating value for the decrease involved in going from the non-planar to planar structure.

Calculations of chemical shifts of the Al^{27} resonance in compounds of aluminum have been made with surprising success. The calculations point out explicitly the consequences of invariance under time inversion on the calculations of chemical shifts (35).

The theory of spin-spin coupling constants has proceeded along fairly well established lines. Conventional valence bond methods have been applied to proton spin-spin couplings in saturated hydrocarbons (36) while a perturbation method has demonstrated that interaction through π -electrons yields couplings over several bonds (37 to 40). Couplings of the order 0.8 sec^{-1} have been found between protons in different rings of aromatic systems (41). Both the π contributions to proton couplings and the C^{13} -H (42) coupling constants are related to the isotropic hyperfine coupling constants in free radicals. For non-rigid molecules, effects of internal motion may be revealed through

dependence of coupling constants on bond angles. Calculations of such effects have been carried forward (43).

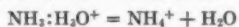
In connection with the high resolution work mentioned in the preceding paragraphs, the description by Turner (44) of the use of the wiggle beat method for detecting very small splittings should be noted.

RATES AND MECHANISMS BY NUCLEAR MAGNETIC RESONANCE

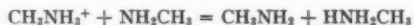
The value of magnetic resonance methods for measuring rates and equilibrium has become so well established that inclusion of a summary of the principles seems unnecessary. Several observations have been made of the rate of transformations between conformational isomers. The chemical shift between axial and equatorial protons in cyclohexane has been observed at low temperatures. With increasing temperatures the lines corresponding to the two sites broaden and finally merge into a single sharp resonance. The process associated with the change in line shape is in all likelihood the chain-chain interconversion in which axial and equatorial protons exchange roles (45). Similar processes have been observed in dithiane (46) and perfluorocyclohexane (47). The chemical shift between fluorines in axial and equatorial positions in perfluorocyclohexane is reported to be 728 sec^{-1} , while in a set of partially fluorinated cyclohexanes, the corresponding shift has been reported to be only about 20 sec^{-1} (48), a rather suspicious discrepancy. The possibility that the apparent equivalence of positions in phosphorus pentafluoride is associated with a rapid interconversion between axial and equatorial positions has been almost eliminated by the observation that the shift is very small in CF_3PF_4 (49).

Investigations of proton transfer processes by NMR are particularly fruitful because of the fortunate sensitivity of line shapes to rates in the range of chemical interest. Meiboom (50) has given a compact summary of the method's range of applicability.

Grunwald and co-workers have made detailed analyses of amine behavior in aqueous solutions. Some of their conclusions do not flow unambiguously from the experimental findings, but all are reasonable. They have determined the rate constants for the reactions (51)



and for (52)



They obtain values in the range 10^{-12} to 10^{-10} sec . (53) for the mean lives of hydrogen-bonded complexes between amines and water.

Proton exchanges in methyl formamide and acetamide (54, 55) have received further study. The equations for connections between line shapes and rates, which are rather complicated except for the simplest limiting cases, are set out in useful form in one study (55).

The exchange of water between bulk solvent and sites close to solute molecules has been studied in several systems. For the paramagnetic ion $(\text{NH}_4)_2\text{C}_6\text{O}^{17}\text{H}_2\text{F}_3$ in solution containing H_2O^{17} , two O^{17} peaks are seen. The resonance of the bound O^{17} is shifted to high field. Addition of paramagnetic ions whose solvation shell exchanges rapidly with the solvent produces a shift of the resonance of the bulk solvent but not of bound molecules. Jackson, Lemons & Taube (56) thus distinguished between the resonance of O^{17} bound to Al^{+++} and that of bulk H_2O^{17} by shifting the latter through addition of rapidly exchanging paramagnetic ions (57). The intensities of the separated peaks yield hydration numbers, and analysis of the O^{17} line shapes will undoubtedly yield exchange rates in many cases of chemical interest. Related information is obtained from relaxation times and chemical shifts of protons in the presence of paramagnetic solutes (57, 58). The rates are almost always so great, relative to the shifts, that separate proton resonances from bound and free water molecules are not seen.

Hertz (59) has made another application of the line broadening method in determining the rate of exchange of bromide ions between symmetrical sites in which the quadrupole interaction is small, and unsymmetrical ones in which it is large.

Only equilibrium properties have been deduced for many processes whose rates lie outside the limits in which the line broadening methods are easily applied. These reactions include: hydrogen bond formation (60) in acids and alcohols (61, 62); formations of proton adducts (63, 64); and formation of complexes of fluoride ions (65), cesium ions (65), cobalt ions (66), and acetaldehyde (67).

STRUCTURE AND MOTION IN SOLIDS

Determining the positions of protons in hydrated crystals (68 to 72) through analysis of the direct dipole splittings remains an active field, as does determining some features of motion through line narrowing. A study by Aston, Stottlemeyer & Murray (73, 74) of the fluorine resonance in CF_4 at various temperatures in the solid and adsorbed states reports the alleged second moments of the absorption line as a function of temperature and infers details of the motion from this "second moment." The conclusions are probably fairly good, but only because both the experiments and the theory are incomplete. The necessity of repeating what should be well known is to be regretted: Many of the kinds of motion that have been reported to change the second moment cannot do so. In particular the contribution to the second moment from the F-F interactions within a CF_4 molecule is invariant to molecular rotation. The second moment seems to diminish with increasing rotation only because contributions from the wings of the line are discarded and a theory that predicts a decrease does so only because it neglects part of the Hamiltonian.

Much recent work on the determination of motion by magnetic resonance utilizes measurements both of the absorption line shape and of the spin-

lattice relaxation time. Maximum use of such data has been made in analyses of motion in silicone plastics (75), ammonium perchlorate (76), adamantane ($C_{10}H_{16}$) (77), and polypropylene polymers (78). A useful calculation of the second moment (not liable to the earlier complaint about the subject) of chains has been made (79). Studies of the proton resonance in zirconium and titanium hydride (80, 81) reveal that diffusion occurs through migration of vacancies. Further, a shift of the proton resonance to high fields indicates that spin density is carried to the protons from the conduction band by an exchange interaction (80).

Although measurements of relaxation times have been used to determine motional behavior in complicated systems, complete understanding of relaxation mechanisms in simple systems has not yet been achieved. Measurements of temperature and field dependence of the spin lattice relaxation time in liquid He^3 (82) appear to have only qualitative agreement with any theory so far applied to them.

In more complex liquids, dependence of relaxation times on concentration, temperature, and pressure indicate participation phenomena associated with mutual rotational viscosity (83) and intermolecular dipolar interactions (84, 85).

Nuclear relaxation processes associated with interactions with paramagnetic impurities are sometimes dominant. A theoretical investigation of the relaxation produced by the diffusion of magnetic energy from a paramagnetic site has been made by Blumberg (86). A demonstration of such interactions, which may have wide experimental application, is the enhancement of C^{13} nuclear resonance through the saturation of electron resonance of paramagnetic impurities (87).

PARAMAGNETIC MOLECULES

The methods, previously used with great success for investigation of paramagnetic ions of the transition elements and rare earths, only recently have been applied systematically to polyatomic radicals. In many instances well-resolved spectra of paramagnetic ions can be obtained only at low temperatures in solid solution in diamagnetic single crystals. The spectra in liquid solutions are often so broad that not much information may be extracted from them. The polyatomic radicals, on the other hand, usually yield better-resolved spectra in liquids than in solids. Much can be learned from the spectra of the liquid solutions, but valuable information dealing with anisotropic components may be almost completely concealed. Despite the difficulties of preparing solid solutions in single crystals and the time consumed in measuring their spectra at many orientations relative to the external field, more such measurements would be valuable and will undoubtedly be performed. In the past year, thorough analyses have been reported of the radicals $HOOCCHCOOH$ (88), $HOCHCOOH$ (89), $HOCHCO_2^-$ (90), $HOCHCH_2COOH$ (91), CH_3CHNH_2COOH (92), and $HOOCCHNHCOOH$ (93), N_4^- (94), produced by irradiation of single crystals of malonic acid,

glycollic acid, glycollates, succinic acid, alanine, acetylglycine, and sodium azide, respectively. Analysis has been made of the nitrogen splitting of diphenyl picrylhydrazyl in single crystals of the diamagnetic diphenyl picrylhydrazine (95). The crystals in the latter case were grown from solution and their composition is quite certain. The identity of the radicals produced by radiation damage must be established from the magnetic resonance spectra; the question of the fate of the products other than the observed radical required by stoichiometry has not always been settled.

The hyperfine splittings in the polyatomic free radicals mentioned in the preceding paragraph are accounted for by the magnetic dipole interaction between electronic and nuclear spins, orbital contributions being of only minor importance. The hyperfine coupling may be summarized as numerical values of the components in a spin Hamiltonian $I_k A_k S$ where I_k is the spin operator for the k^{th} nucleus, A is a tensor whose components are usually given in a coordinate system attached to the crystal, and S is the electronic spin operator. The components of each A_k may be identified with the expectation values of components of the dipole-dipole operator. If the hyperfine splitting may be represented as arising from the interaction of a single electron with the nuclei, the trace of each A_k yields the expectation value of δ ($r-r_k$), i.e., the density of the electron at the position of the nucleus. The individual entries in A_k yield expectation values of r^{-3} , $1-3 \cos^2 \theta$, $\sin \theta \cos \theta e^{i\phi}$, and $\sin^2 \theta e^{2i\phi}$; θ and ϕ are polar angles of the electron-nucleus vector relative to the axes in which A is given; r is the nucleus-electron separation. If the orientations of the radicals in the crystal are known, the expectation values may be found relative to molecular axes. In many electron systems the entries in the coupling tensor are expectation values of corresponding sums over all the electrons.

The authors of the investigations described in the preceding paragraphs (88 to 94) have noted that the Hamiltonian is not diagonal in the states corresponding to quantization along the external field. Zeldes, Trammell, Livingston & Holmberg (96) have administered a more or less deserved scolding to those (including me) who failed to include the necessary off-diagonal terms in analyzing spectra of crystals. Under conditions frequently encountered, the dipolar magnetic field at a nucleus is of the same order as the external field and is not parallel to it; the component of nuclear spin along the external field is not a good quantum number. Further, the nuclear spin eigenstates are not the same in the two (or more) electronic spin eigenstates because of the differences in direction of effective fields at the nuclei. Because of the lack of orthogonality between the nuclear spin parts of the eigenfunctions, transitions forbidden in the scheme of quantization appropriate for liquids (or very high fields) may acquire appreciable intensity. A striking example is seen in the radical derived from malonic acid (88). Only one proton produces appreciable hyperfine splitting, yet four electron resonance lines of equal intensities are seen at some orientations. At such orientations the effective fields at the proton in the two electronic spin states are perpen-

dicular to each other and the integrals between pairs of nuclear spin functions are equal. The phenomenon is analogous to the appearance of many vibrational bands in the electronic spectrum of a polyatomic molecule when the vibrational Hamiltonians in the two electronic states are not the same.

SIGNS OF HYPERFINE COUPLING CONSTANTS

The results, already described, from investigations of the radicals derived from radiation damage to simple organic acids (88 to 93) have one feature in common: each radical is characterized by strong anisotropic as well as isotropic interactions of a single proton with the electronic spin. In alanine the electronic spin also interacts further by an almost completely isotropic coupling with three equivalent protons, while in succinic acid additional isotropic interaction occurs with two equivalent protons. In each case the anisotropic (trace=0) part of the coupling tensor with the unique proton corresponds to the dipolar interaction with an electronic magnetic moment distributed in a p orbital centered on the carbon atom adjacent to the proton. The axis of the p orbital is normal to the bond direction. The magnitude of the isotropic interaction is in the range 20 to 25 gauss, close to the total proton splitting in many aromatic radicals. Further, the isotropic and direct dipolar components of the interaction have relative signs opposite to those calculated for a single electron in a mixed s - p orbital, this is in agreement with those calculated for an isotropic interaction whose origin is an exchange interaction in a many-electron system.

The analysis of the spectra of diphenyl picrylhydrazyl in solid solution (95) has yielded the coupling tensors with the two hydrazine nitrogens. Earlier experiments with liquid solutions had suggested that the isotropic coupling constants with the two nitrogens were equal, but more careful analysis yields a ratio of 0.82 between them (97). The latter value is not in very good agreement with the one deduced from the spectra of the crystals; the discrepancy may arise from systematic errors in analysis of the data or from real effects of environment on the splittings.

The two nitrogens differ not only in the numerical values of the components of their coupling tensors, but also in the orientations of the principal axes, the angles between the three corresponding tensor axes, and a crystal axis differing by 6.5, 6.0, and 11.9 degrees. The relative signs of isotropic and anisotropic components correspond to those arising from single occupancy of a mixed p - s orbital, but the results need not be so interpreted. Exchange interactions are more complex for many electron atoms than for hydrogen, and either sign of isotropic coupling may arise.

The isotropic N^{14} and N^{15} splittings have properties in common with those of C^{13} . Several instances of C^{13} splittings, both from isotopically enriched materials and from those containing the isotope in natural abundance have now been reported (98 to 103). The sign of the spin density at the carbon atom in the radical derived from malonic acid is positive (98). An earlier study of triphenylmethyl had suggested negative spin density at the methyl

carbon. This result should be checked, since it is not easily reconciled with the more reliable observations in malonic acid.

Many radicals of interest can be produced only in random orientations in solids. Several papers have dealt with the problem of extracting coupling constants and g values from the spectra of such randomly oriented radicals (104 to 108).

The study of radicals produced in solids by maltreatment of one kind or another continues to be an active field. A thorough investigation of the several species of radicals produced by irradiation of polyethylene with 800 kv electrons has produced valuable information concerning possible identification of the radicals and their interactions with their environments (109, 110). Spectra have been reported from irradiated polyvinyl chloride (111), polytetrafluoroethylene (112, 113), hydrogen bonded polymers (114), silica gel (115), tetraalkyl halides (116), and oxalic acid (117). Charred dextrose yields an easily prepared inhomogeneously broadened line (118). Uncertainties persist concerning the identity of the radicals produced by irradiation of ice (119, 120). A doublet at $g=2$ with splitting of 40 gauss has been ascribed to OH (120), although in the gaseous state the g values are far from 2 (121). Experiments with D_2O confirm that a single hydrogen is responsible for the splittings but do not identify the radical. The colored forms of sulfur produced by condensation of sulfur vapor on a chilled surface are paramagnetic, but no identification has been achieved (122).

A study of hydrogen atoms trapped in solid rare gases has demonstrated some of the effects of the environment on magnetic resonance spectra. The hyperfine couplings with the proton and g values vary from one medium to another. Small couplings with the nuclei of xenon are observed (123). The effects have been accounted for through van der Waals and overlap interactions between the hydrogen atoms and the matrix. The g -value shifts are associated with spin polarization on the heavy atoms of the matrix where spin orbit interactions become effective (124).

LIQUID SOLUTIONS

Significant advances have been achieved during the past few years in the resolution of ESR spectra of liquid solutions. The improvement has resulted from progress in understanding the line broadening mechanism and in the design and construction of spectrometers. As the sensitivity of spectrometers is enhanced, the concentrations at which radicals may be conveniently observed is diminished, with a corresponding narrowing of lines. Even at the lowest concentrations detectable by current models of spectrometers, broadening through intermolecular perturbations may be significant. Although line breadths in very dilute solutions would be expected to diminish monotonically with decreasing viscosity, observations usually have shown that as viscosity increases the line breadths of individual lines decrease, pass through a minimum, and then finally increase. As the concentration is decreased, the viscosity at which the minimum line breadth occurs is also decreased. Clearly,

intermolecular interactions associated with motions of free radical molecules relative to each other contribute to line breadth, and these may be diminished with increasing viscosity (125, 126, 127). Broadening by interaction with dissolved oxygen can be reduced by increasing viscosity, or eliminated by removing the oxygen (128, 129).

Kivelson (130) has applied the general methods of Kubo and Tomita to the calculation of line shapes in ESR spectra. His work takes account of intermolecular exchange, g values, and dipolar interactions and anisotropies in hyperfine couplings. Other contributions to the same topic have treated the problem by less general methods (131) and have indicated how the relaxation parameters T_1 and T_2 may be determined through dependence of both the breadth and intensity of the lines on the intensity of the oscillating field (132). Measurements of the polarization of nuclei in the solvent, by saturating a transition in dissolved $\text{NO}(\text{SO})_2^-$ with both transverse and longitudinal oscillating fields, reveal that the mechanisms included in Kivelson's treatment can be responsible for only a small fraction of the line breadth (133). The measurements do not indicate that the contributions of the various mechanisms included in the theory have been incorrectly estimated; they indicate that other mechanisms probably participate. Similar conclusions have been drawn from studying the breadths of the hyperfine components of VO^{2+} . The variations in line breadth are accounted for by theory, but the total breadths are not (134). One is tempted to assign all the unaccounted-for line breadths to spin orbit interactions, but until more direct evidence than has yet been presented is found, the possibility of intervention of mechanisms not yet recognized should not be dismissed. Orbital degeneracy is probably involved in the anomalously broad line and enhanced spin-lattice relaxation of the negative ions of benzene, coronene, and triphenylene (135). Theoretical work by McConnell & McLachlan (136) and by McConnell (137) suggests that spin orbit interaction rather than the dynamical Jahn-Teller effect produces the broadening.

ANALYSIS OF WELL-RESOLVED SPECTRA

Analysis of a well-resolved ESR spectrum consists of an attempt to find a set of coupling constants that represent the spectrum and a theory that yields an explanation of the coupling constants. Because of the difficulties associated with analyses of complex spectra, the two tasks are not independent; the results of one are used to refine the other. Consider a typical case, that of the negative ion of $\alpha\alpha'$ binaphthyl. The spectrum could have 375 lines if there were no accidental coincidences. Well over 200 have been observed by M. Townsend. Molecular orbital calculations of the kind that have been successful for simpler radicals have provided estimates of the seven required coupling constants, and high speed computing techniques have been used by L. Snyder to construct the spectrum led to by the coupling constants. Comparison of the calculated and observed spectra is frustrating since, while clear discrepancies are apparent, there is no reliable method for

estimating the errors in coupling constants that would lead to the observed discrepancies. If a set of coupling constants yields agreement between observed and computed spectra, the constants are probably correct, but discrepancies may be produced by a small error in one coupling constant. Either more extensive use of isotopic substitution or exploitation of techniques such as Endor, and direct measurements of nuclear resonance, or the invention of new computational methods are necessary for extensions to large molecules of the methods that have been valuable for small ones.

The theoretical work on hyperfine coupling constants has proceeded in the main along two almost independent paths. One path maps out the principal features of spin distribution while the other establishes the relations between this spin distribution and spin densities at particular nuclei. A complete solution of the first problem would include the results sought in the second, and in a few investigations the two aspects of the problem have been treated together (138, 139, 140). Spin densities at nuclei are often small compared with densities at other places and are usually obtained by a perturbation treatment that starts with a specification of where most of the spin is.

An extended theory of the first kind uses functions not restricted to the same space function with each pair of opposed spins (141). The component of appropriate multiplicity must be projected out of the unrestricted function. Such unrestricted functions lead naturally to the alternation in sign of spin densities. The method is almost equivalent to the use of a self-consistent molecular orbital treatment with inclusion of the appropriate configurations having three singly occupied orbitals for systems with $S = \frac{1}{2}$ (142).

Work on the second aspect of the theory has advanced to include consideration of spin densities at heavier nuclei such as carbon and nitrogen, as well as hydrogen. The theory of the splittings by carbon and nitrogen in aromatic systems has been worked out along the same lines as the earlier work on proton splittings (143). The theory derives proportionality between spin density on carbon atoms and splitting by adjacent protons with less restrictive assumptions than previously used, and it finds similar but more complicated relations for carbon and nitrogen. The isotropic coupling constant of an aromatic carbon or nitrogen appears to have a positive contribution proportional to the spin density on the atom in question and negative contributions proportional to the densities on the neighboring atoms. A calculation of the hyperfine coupling in atomic nitrogen ($^4S_{3/2}$), where spin is carried from p orbitals to the nucleus by processes similar to those involved in aromatic radicals, yields a positive coupling constant (144).

Certain limitations arise in the use of the spin density concept for describing observed isotropic hyperfine interactions. Usually the isotropic coupling constant with a particular nucleus may be identified with the time average of the spin density at that nucleus. The procedure is justified when the matrix elements of the hyperfine interaction operator are small compared with the energy differences between the eigenstates of the rest of the Hamiltonian, i.e., when the hyperfine interaction does not affect the electron distribution. But if orbital degeneracies or near degeneracies exist, the hyperfine

interaction itself may be dominant in determining the spin distribution. Thus if a single electron has two equivalent sites accessible to it, the stationary state functions are, in the absence of hyperfine interaction, either symmetric or antisymmetric in the site, with probability distribution symmetric in the sites. But if nuclear moments are situated at the sites, the hyperfine interaction may mix the orbitally symmetric and antisymmetric states. If the hyperfine interaction is large compared with the orbital interaction, the observed hyperfine splitting would correspond to the electron being at one or the other site and not to the average distribution over a long period of time. ("Long time" means many periods of the hyperfine precession.) Such cases have been observed in the ions of the paracyclophanes and certain polyphenyls where the hyperfine splitting corresponds to interaction with nuclei in half of a symmetrical molecule.

While instances are rare in which orbital interactions are so small that they may be interfered with by hyperfine interactions, they should not be disregarded, since they correspond to rates that lie in a region of chemical interest. In the negative ion of diphenylethane, as an example, the orbital interaction between the symmetric and antisymmetric distribution in the two rings is clearly large when compared with the proton hyperfine interactions (145).

The work on ESR spectroscopy of most radicals has been marked by unusual agreement among the spectra reported by different workers for various radical species. An interesting exception has appeared in the spectra of radicals produced by reduction of aromatic nitro compounds. The radical produced by electrolytic reduction of nitrobenzene in acetonitrile is characterized by a set of coupling constants that agree well with those of the radical formed by reduction with potassium in ethers (146). But in the corresponding experiments with metadinitrobenzene, a radical that had equal coupling constants to two nitrogens was formed in the electrolytic reduction, while a radical with coupling to only one nitrogen was formed by chemical reduction (147, 148). The coupling constant for each of the two equivalent nitrogens in the electrolytic experiments is 4.68 gauss, and for the single nitrogen in the chemical experiment, 9.0 gauss. It has been suggested (147) that the chemical reduction leads to decomposition with loss of one nitrogen atom from the molecule, but it appears likely that ion-pair formation is responsible. Numerous experiments in which hyperfine couplings to alkali metal nuclei are resolved have shown that the radicals produced by the ether solvents through reduction with alkali metals contain one alkali metal atom per radical. Electrostatic interaction with the cation may produce redistribution of spin corresponding to the observed spectrum. Suppose that the free ion of meta dinitrobenzene may be described by a function that is either symmetric or antisymmetric with respect to exchange of the spin between the two nitro groups. Interaction with the cation mixes the antisymmetric and symmetric states to yield states in which the spin densities on the two nitrogens are no longer equal. The experiments demonstrated that the coupling constant with one nitrogen must be less than about 0.1 gauss. If the

splitting between symmetric and antisymmetric states in the absence of the perturbing ion is Δ , the magnitude of the interaction V that will reduce the coupling constant from 4.5 to less than 0.1 gauss is given by $V^2 > 4.5/0.1 \Delta^2$. If the above explanation is correct, the free ion would be expected to have an intense electronic absorption in the infrared.

The redistribution of spin on ion-pair formation requires the existence of closely spaced and easily perturbed levels. Such levels are not present in the naphthalene negative ion where ion-pair formation produces no measurable redistribution of spin.

Greatly improved spectra of radicals that were studied in the past have been reported. The 1960 model of the spectrum of the oldest stable free radical, triphenylmethyl, is almost completely resolved (149) and indicates that simple valence bond theory, while coming close, is not entirely adequate. The spectrum of another venerable radical, Wurster's blue, has now been completely resolved (129). The couplings to the nitrogen are much smaller than theoretical estimates thus far made.

One aspect of ESR spectroscopy that contributes to its increasing use is its self-nourishing property. The method discovers new radicals or confirms the presence of others whose existence could only have been conjectured without spin resonance. Thus, the existence of a steady concentration of ethyl radicals in liquid ethane under excitation by 2.5 Mev electrons has been demonstrated (150). From estimates of the concentration of the radicals and the rate of their production, the authors determined a mean lifetime of the radicals. An estimate from the line breadths of their published spectrum sets a somewhat longer upper limit.

A new series of radicals formed by reduction of tetracyanoethylene and its derivatives has been discovered (151). The spectrum of $(\text{CN})_2\text{C}=\text{C}(\text{CN})_2^-$ in dilute solution shows the expected pattern from four equivalent nitrogens, in addition to weaker lines from the natural abundance of N^{15} and C^{13} . New phenoxy radicals (152), vinyl anion (153), fluorinated semiquinones (154), radicals containing aluminum (155), and phototropic substances (156) have been described.

The discovery of the cyclooctatetraene anion radical by Katz & Strauss (157) is of particular interest because of its bearing on problems associated with connections between structure and hyperfine splittings. Reduction of cyclooctatetraene by alkali metals leads mainly to a dinegative diamagnetic ion. A small concentration of radical with eight equivalent protons is in equilibrium with cyclooctatetraene and its dinegative ion. The total splitting is about 25 gauss, about equal to the value found in aromatic radical ions. The result suggests that the proportionality constant between π density and proton splitting is insensitive to the bond angles at the carbon atom.

INORGANIC IONS

The study of paramagnetic compounds of transition elements, rare earths, and transuranic elements has continued, although perhaps not at the rate of a few years ago. Only a few cases will be described here.

Investigation of the spectra of a copper porphyrin in solutions of various viscosities has permitted a sifting out of almost as much information as is usually attained from dilute single crystals (158). Spin density is found at the nitrogen nuclei of the ligands.

Thorough studies of the manganate (MnO_4^-) and ferrate (FeO_4^-) ions have been made (159, 160). Single crystals of potassium chromate serve as diamagnetic hosts; the site symmetry is not tetrahedral. Earlier work on the optical spectra of manganate ion had not yielded unambiguous classification of its electronic states. The ground state could have been either of *E* or *T* symmetry. The magnetic measurements are compatible only with the *E* classification. The ground state of ferrate ion is an almost pure triplet, with small zero field splittings arising from electronic spin-spin dipolar interaction.

Several investigations have dealt with the ESR spectra of manganous ion in various environments. Hyperfine splitting is produced not only by interaction with the nuclear moment of manganese but with halogen nuclei as well. A remarkable variety of complexes has now been observed (161 to 165). The resonance at $g=4$ in ferric ion in glass has been traced to a large zero field splitting (166). The second order effects in the complex FeF_6^{3-} , similar to those already described for organic radicals, have been unraveled (167). Parameters in the spin Hamiltonian have been determined for titanium, chromium, and ferric ions in aluminum chloride hexahydrate (168). Cobalt ion in the cubic environment provided by cadmium fluoride and cadmium telluride exhibits a pronounced contribution to the hyperfine splitting through coupling of the orbital electronic magnetic moment with the nuclear moment (169). Resonance has been observed from the tetra-positive oxidation state of protactinium in cesium zirconium fluoride, where a large orbital contribution to the magnetic moment is observed. The hyperfine splitting demonstrates that the nuclear spin is $\frac{3}{2}$ (170). A remarkably isotropic spectrum is displayed by neptunium hexafluoride in solution in single crystals of uranium hexafluoride (171). The spectrum is consistent with the configuration f^1 in an octahedral environment with large spin orbit interaction. The well-resolved hyperfine splitting by the fluorine nuclei has not yet been used for analyzing the nature of the chemical bonding.

TRIPLETS AND BIRADICALS

States of various multiplicities have been studied among the inorganic paramagnetic species since the early days of magnetic resonance. But among the polyatomic organic free radicals, the work had been restricted either to pure doublet states, i.e., dilute solutions of free radicals, or to systems of many and high multiplicities—the pure crystalline free radicals. The simplicity of the single exchange narrowed lines near the free electron g value of the crystalline radicals may be deceptive. Exchange and dipolar interactions operate in such a way that only the transitions corresponding to absorption or emission of one quantum of Zeeman energy are observed among the almost continuous array of states that exist in the crystal.

Only recently has the magnetic resonance of a complex triplet molecule

been observed by Hutchison & Mangum (172, 173). The elegant single crystal method used for observing the photo-excited state of naphthalene is not easily applied to many other triplets of interest because it is difficult to obtain comparable molecular alignment. Recognition by van der Waals & de Groot (174, 175) that the transitions with $|\Delta m| = 2$ may be observed for triplet molecules in random orientation in rigid media will undoubtedly lead to measurements of many more triplet molecules. Because of the prospect of extensive use of the method, its principles are sketched out in the following paragraphs.

The eigenstates of the Zeeman part of the Hamiltonian ($m = -1$, $m = 0$, $m = 1$) are convenient zeroth order functions. The diagonal part of the dipole-dipole interaction is

$$\mu_0^2 \sigma_{iz} \sigma_{jz} \frac{(1 - 3 \cos^2 \theta_{ij})}{|r_{ij}|^3}$$

when μ_0 is the Bohr magnetron, σ_{iz} the Pauli operator for the z component of spin of the i^{th} electron, r_{ij} the vector between electrons i and j , and θ_{ij} the angle between r_{ij} and the axis of quantization. Since the first order correction depends only on the mutual orientation of a pair of electron spins, it is the same for $m = +1$ and $m = -1$. Hence in first order the interval between the two states does not change with orientation. On the other hand, the state with $m = 0$ is always displaced in the opposite direction from the $m = \pm 1$ states.

The off-diagonal elements of the Hamiltonian contain products of spin operators of the form $\sigma_{iz} \sigma_j^+$, $\sigma_{iz} \sigma_j^-$, $\sigma_i^+ \sigma_j^+$, and $\sigma_i^- \sigma_j^-$ (σ^+ and σ^- are raising and lowering operators). The first two of these operators mix $m = 0$ with $m = \pm 1$ and the other two mix $m = +1$ with $m = -1$. The admixture of $m = 0$ into $m = \pm 1$ permits absorption of radiation with the oscillating component of magnetic field H_1 perpendicular to the static field. The admixture of $m = \pm 1$ into $m = 1$ permits transition by radiation with H_1 parallel to the static field. By studying spectra at the two polarizations, almost as much information can be obtained about the dipolar interaction as from noting the angular variations of the absorption in single crystals.

The method has been applied to the triplet states of coronene, triphenylene, 1,3,5-triphenylbenzene, and naphthalene (175). Despite strenuous efforts, magnetic resonance of the triplet state of benzene has not been reported (or observed to my knowledge).

The information obtainable from the magnetic resonance of triplet molecules is, or ought to be, of great interest to those concerned with theories of electronic structure because of the dominant effects of electron correlations. Expectation values of operators, which involve pairs of electrons, emerge almost directly from the measurements. In addition, the hyperfine splittings will yield parameters similar to those obtained for doublet molecules.

Progress toward explaining the spin-spin splittings has been made (176, 177, 178). It is too early to say which features of the standard chemical ap-

proximations will survive the stringent tests provided by the experiments. Natural orbital expansions and density matrix methods will probably prove useful in the theoretical work.

Another group of even electron paramagnetic molecules, the biradicals, has been studied using the methods of magnetic resonance. The term "biradical" has sometimes been used to include triplets, but it might be well to reserve it for those even electron paramagnetic molecules whose properties are represented by superpositions of triplet and singlet functions corresponding to independent spins in two parts of the molecule. Experiments designed to determine the coupling between spins in a series of biradicals have been carried out. A series of four compounds consisting of pairs of triphenylmethyls joined in various ways has been synthesized with C^{13} in the methyl position. In each case the liquid solutions of the radical revealed extensive and well-resolved proton hyperfine splittings, and large C^{13} splittings similar to the interaction of each unpaired electron with one C^{13} (179). The results correspond to interactions between electron spins much smaller than the C^{13} hyperfine interaction of seventy megacycles. The stationary states required for description of the observed spectra are eigenfunctions not of the square of the electronic spin angular momentum, but rather of the total spin angular momentum, electronic and nuclear. The electron spins are more strongly coupled to the nuclei than to each other. Theoretical calculations predict couplings in rigid molecules much larger than those observed (180). McConnell (181) has suggested that during intramolecular rotations the molecules are found in intermediate spin decoupled configurations for times sufficiently long to give the observed spectra. Further chemical work to determine the identity of the absorbing species and to prepare new biradicals is necessary. Elucidation of the behavior of charge transfer complexes (182) as well as the weak interactions between pairs of paramagnetic ions (183) is undoubtedly relevant. Double resonance experiments designed to detect weak couplings will probably be helpful.

NUCLEAR RESONANCE OF PARAMAGNETIC MATERIALS

The phenomena reviewed in the preceding section are associated primarily with electron spin transitions. We turn now to experiments in which, while the substances under investigation are electronically paramagnetic, nuclear spin transitions are observed. The nuclear spin transitions may be observed directly or through their effect on electronic absorptions, as in the Endor method. An enlightening application of the latter technique has been made to the paramagnetic centers produced by irradiation of lithium fluoride. The Endor experiments are accounted for by interaction of the center with the eight layers of nuclei around it (184).

Direct observations of nuclear resonance absorption in paramagnetic molecules has been particularly useful in measuring the signs of hyperfine coupling constants. The sign of a coupling constant with a particular nucleus depends on the mechanism by which the spin density is produced. Thus the

π - σ interaction, which is responsible for the isotropic proton splittings in aromatic systems, leads to the spin at each proton being in an opposite direction to that at the adjacent carbon atom. In complexes of transition elements the signs of spin densities at ligand positions depend on the nature of the bonding.

The principles of the nuclear resonance method for determination of signs as well as magnitudes of coupling constants have been known since the discovery of the Knight shift. The measurements are carried out under conditions in which sharp averages over the various electronic Zeeman levels are observed. The contribution of each electronic Zeeman level being weighted by its Boltzmann factor, the effects are enhanced by decrease in temperature. Sharp averaging is accomplished by rapid electron exchange or spin lattice relaxation. The method was applied to crystalline diphenyl picrylhydrazyl by Anderson, Pake & Tuttle (185) and later by others (186, 187), where the alternating signs of spin density expected for odd alternant radicals are observed. The method has been especially successful for pyrene negative ion, an even alternant radical whose ESR spectrum does not agree with predictions of simple Huckel theory. The spin densities are negative at two proton sites, positive at the third (188). The results are consistent with highly resolved ESR spectra obtained in liquids (189) and with calculations carried one order beyond the simple Huckel theory (142).

Averaging over the Zeeman levels through rapid spin lattice relaxation is effective in chelates of the transition metals. The proton resonances in liquid solutions are remarkably sharp and display shifts much larger than normal chemical shifts. Alternating signs of spin density are vividly displayed in the experiments of Phillips & Benson (190). The success of the method depends on a relaxation of the electronic paramagnetism rapid enough to be rather ineffective in producing nuclear relaxation.

Further observations of shifts in inorganic compounds have been made for the fluorine resonance in FeF_2 (191) and in KMnF_2 (192), the cobalt resonance in CoO (193), and rare earth nuclei in various intermetallic compounds (194). In the latter case the spin density is carried to the nuclei by an exchange interaction between $4f$ electrons and conduction electrons; the exchange energy is negative.

APPLICATION TO BIOLOGICAL SYSTEMS

Increasing use of resonance methods for investigations of biological problems may be expected. The work reported thus far has ranged from studying pure compounds of biological importance to intact living systems. The P^{31} resonances of the phosphates of adenosine are sensitive to pH and other environmental variables (195). Commoner & Hollocher (196, 197, 198) have studied a free radical intermediate in mixtures of succinate and fumarate. The radical is produced in the presence of mitochondria or purified succinic dehydrogenase. From noting the dependence of radical concentration on temperature and concentrations of reagents, much information concerning

stoichiometry and thermodynamic constants has been obtained. Finally, ESR has been observed from living chlorella (199). Complex dependence of resonance on many variables such as light intensity, nutrient medium, and history are observed. Of particular interest for identifying the radical species is the dramatic effect on the line shapes when chlorella grown in a deuterium oxide medium is utilized.

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ELECTROLYTE SOLUTIONS¹

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STATISTICAL MECHANICS OF ION INTERACTION

A persistent duality in chemistry is found in the alternative chemical and physical interpretations used when chemical systems deviate from some assumed ideal behavior. A particular form of this duality appears in several papers reviewed here: When is deviation from ideal behavior by the properties of an electrolyte solution to be attributed to the association of ions into pairs or larger clusters, and when is it attributable to the effect of long-range forces over and above those accounted for by the limiting Debye-Hückel theory?

In a novel approach to this problem Guggenheim (1) points out that the second virial coefficient b_{ij} is always clearly defined and is indistinguishable from K_{ij} , the equilibrium constant for association of i with j , when K_{ij} is clearly defined by the usual criteria.² We have

$$b_{ij} = \frac{1}{2} \int_0^\infty [\exp(-u_{ij}/kT) - 1] 4\pi r^2 dr \quad 1.$$

which is the second virial coefficient of the pressure of a gas or of the osmotic pressure of a solution, depending on whether $u_{ij}(r)$ is the potential of the interaction of molecules i and j at separation r in the vacuum or in the pure solvent. Also $K_{ij} = c_{ij}/c_i c_j$, where c_i is the number of molecules of species i per unit volume. The problem of establishing c_{ij} in difficult cases may be circumvented by using b_{ij} instead of K_{ij} .

For ionic systems the integral 1 does not converge, and it is proposed to replace it by the "degree of supersatiation"

$$b_{ij}^* = [(c_i + c_j)/2] \int_0^\infty [\exp(-w_{ij}/kT) - e^{q_{ij}}] 4\pi r^2 dr \quad 2.$$

where $-kTq_{ij}$ is the Debye potential,

$$q_{ij} = -z_i z_j e^2 e^{-\kappa r} / DkT r \quad 3.$$

and $w_{ij}(r)$ is the potential of average force for the pair of ions at separation r in the solution. To apply Equation 2, the w_{ij} may be obtained from a complete numerical solution of the Poisson-Boltzmann equation (2, 3) for the primitive model (defined below). These w_{ij} lead to osmotic coefficients in good agreement with experiment (3); with them and Equation 2 it is concluded, for example, that one need not invoke association to interpret the free energy data for aqueous CuSO_4 solutions. This is in contrast to the conclusion drawn

¹ The survey of literature pertaining to this review was concluded December 1, 1960.

² The same notation is used throughout this section.

from some other methods of treating similar data that lead to association constants as large as 230 for the same system (4). Of course the primitive model and the Poisson-Boltzmann equation are inaccurate and it is conceivable that an accurate w_{ij} , also in accord with the osmotic coefficients, would be different enough from Guggenheim's to lead to an appreciable "degree of supersatiation" of Cu^{++} and SO_4^{--} . Therefore, the question as to whether the chemical approach is misleading in this instance is still open.

A wider view of this important problem must include nonthermodynamic observations that are frequently adduced as evidence for molecular association. An elegant approach is illustrated by van Kranendonk's study (5) of the new infrared absorption that appears when mixtures of H_2 and Ne are compressed. This is due to a transition forbidden in the isolated H_2 molecule but allowed in perturbing fields such as that supplied by a nearby Ne atom. The intensity of the absorption is therefore proportional to

$$c_{ij}c_j \int_0^\infty p_{ij}g_{ij}4\pi r^2 dr \quad 4.$$

where $p_{ij}(r)$ is the probability for the transition in the field due to a Ne atom at distance r from the H_2 molecule, and

$$g_{ij}(r) = \exp(-w_{ij}/kT) \quad 5.$$

is the correlation function (radial distribution function) for a pair $\text{H}_2\text{-Ne}$ in the compressed gas. There is sufficiently detailed information about both p_{ij} and g_{ij} in the systems van Kranendonk investigates to allow a quantitative interpretation of the data in terms of molecular parameters. On the other hand, the usual chemical approach would lead one to assume a "complex" of composition H_2Ne with appropriate spectral properties.

Considering more conventional aspects, Falkenhagen & Kelbg (6), in a critical review of the statistical theory of ionic interaction, include an outline of the Bogoliubov theory as well as a new approach to an equilibrium theory for the low concentration range (7). The central equation is

$$w_{ij} = u_{ij} - kT \sum_s c_s \int f_{is} [g_{js} - 1] d\{1_s\} + \dots \quad 6.$$

where the symbols have been previously defined except $\{1_s\}$, the spatial coordinates of a molecule of species s , and

$$f_{is} = \exp(-u_{is}/kT) - 1 \quad 7.$$

The neglect of the unspecified terms in Equation 6 has not been justified in detail, but they do all involve higher powers of the c_s . It is interesting to note that a more accurate equation of similar form is readily obtained from a result of Meeron's (8) by neglecting higher powers of the c_s . It is

$$w_{ij} = \bar{u}_{ij} - kT \sum_s c_s \int [(g_{is} - 1)(g_{sj} - 1 - q_{sj}) + (g_{is} - 1 - q_{is})(g_{sj} - 1)] d\{1_s\} \quad 8.$$

where, if we define u_{ij}^* as the short-range part of the direct potential

$$u_{ij}^* = u_{ij} - z_i z_j e^2 / Dr \quad 9.$$

then the shielded direct potential is

$$\bar{u}_{ij} = u_{ij}^* - kTq_{ij} = u_{ij}^* + z_i z_j e^2 e^{-kr} / Dr \quad 10.$$

Kelbg (9) has obtained a solution of Equation 7 not only for the primitive model $u_{ij}^*(r) = \infty$ if $r < a$, $= 0$ if $r > a$ but also for the square-well model (10) characterized by

$$u_{ij}^*(r) = \infty \quad \text{if } r < a, \quad u_{ij}^* = -h \quad \text{if } a < r < 2a, \quad u_{ij}^* = 0 \quad \text{if } 2a < r.$$

This is of great interest because it allows us to represent a short-range attractive potential without sacrificing much of the simplicity of hard sphere models. In the present case h includes both attractive and repulsive contributions of the solvent to the short-range part of the direct potential as well as a contribution from the mutual polarization of the ions.

The calculations lead to expressions for the osmotic coefficient in terms of a and h . Comparison (11) with data for Bu_4NCl and Bu_4NI shows good agreement up to 0.04 molal with $a = 7\text{\AA}$ for both, and with h/kT equal to 0.16 for the former and 0.36 for the latter. Although the chloride and iodide show strong deviations from the limiting law in opposite directions, both are accommodated within this small range of h .

The square-well model ought to have wide applicability to ionic solutions but it is to be expected that three parameters (h , a , and the other distance which Kelbg sets at $2a$) are too many to determine uniquely by comparison with experiment. Therefore, it is important to find restrictions on the ranges of the parameters by calculating u_{ij}^* from a reasonable model. One approach to this difficult problem is to assume that around each ion there is a first solvation layer with limited freedom of motion and to represent the rest of the solvent as a homogeneous dielectric (12), another is to represent the solvent as a continuous medium with a field-strength dependent dielectric constant (13, 14), but further work is required on this.

The virial equation for the pressure of an imperfect gas is of course just a Taylor series expansion in powers of the molecular concentrations. The cluster theory of statistical mechanics provides an expression for the n th virial coefficient in terms of the interactions among just n molecules. If some of the molecules are charged, these expressions lose their meaning, but by rearranging the terms of all of the virial coefficients Mayer (15) obtained a new expansion similar to the virial except that it is valid for ionic systems and has coefficients that are not independent of the concentrations. Mayer assumed that the direct potentials are only pairwise: For n ions in the solvent at coordinates $\{n\}$ the potential energy of interaction may be expressed as a sum of pairwise contributions,

$$U_n(\{n\}) = \sum_{\text{pairs}} u_{ij}(r_{ij}). \quad 11.$$

Friedman (16) removes this restriction, which limits the models to which the

theory can be applied, and collects the higher terms of the expansion to obtain an equation that is most simply written as

$$-F^{\text{ex}}/kT = \kappa^3/12\pi + \sum_{n \geq 2} c^n B_n(\kappa) \quad 12.$$

where F^{ex} is the excess Helmholtz free energy per unit volume. The coefficients $B_n(\kappa)$ are similar to virial coefficients in depending on U_n but are also functions of the Debye κ . Even for the simplest direct potentials $B_n(\kappa)$ can be evaluated by elementary methods of numerical integration only if $n=2$. Equation 12 is usually more convenient for comparison with experiment than the corresponding equation for the osmotic pressure, although the latter is more closely related to the virial equation.

Questions of convergence of the series in Equation 12 are troublesome, but it is at least clear that as $\kappa \rightarrow 0$ the first term (Debye-Hückel limiting law) is largest, the sub-sum for which $n=2$ is next largest, etc. (17).

The form of Equation 12 at once suggests its application to electrolyte mixtures, for in a mixing process at constant κ the $B_n(\kappa)$ behave like constant coefficients. An investigation of this aspect (18) elucidates the properties of the excess free energy of mixing at constant ionic strength, $\Delta_m G^{\text{ex}}$ (see below). The most striking result is that for a mixture of two electrolytes of the same charge type, say $A_m X_n$ and $B_m X_n$, the leading term in $\Delta_m G^{\text{ex}}$ has the coefficient

$$\int_0^\infty [\exp(-u_{aa}^*/kT) + \exp(-u_{bb}^*/kT) - 2 \exp(-u_{ab}^*/kT)] c^{aa} 4\pi r^2 dr.$$

Thus, $\Delta_m G^{\text{ex}}$ is a measure of the differences in short-range interaction among like-charged ions. At another extreme is the application of Mayer's theory to the hypothetical one-component ionic gas (19) where the initial simplicity allows some aspects to be investigated in great detail.

The numerical inconsistency of the Poisson-Boltzmann equation for unsymmetrical electrolytes has been evaluated (2) and found to be appreciable. On the other hand Frank & Thompson (20) find that for any electrolyte the validity of the Poisson-Boltzmann equation is assured only if $c = c_+ + c_- < \kappa^{-2}$, which for aqueous 1-1 electrolytes at 25° corresponds to ionic strength $I < 10^{-3}$ molal. It is also suggested that at higher concentrations $c^{-1/3}$ may take the place of κ^{-1} as the ion-atmosphere radius, implying that the distribution of ions in the solution approaches that of an expanded ionic lattice with parameter about $c^{-1/3}$, just as in the old Ghosh theory. In support of this it is noted that the experimental $\log \gamma_{\pm}$ is linear in $c^{1/3}$ through a considerable range above $I = 10^{-3} M$ for many salts. It is intriguing to note that a development (21) of Kramers' theory shows a transition from $c^{1/2}$ to $c^{1/3}$ dependence, but at a somewhat higher concentration.

A further basis for expecting a lattice-like structure in concentrated ionic solutions is found in the investigation (22) of a variation of the Kirkwood integral equation for a simple model of a fused salt. Two such equations are added to get an equation for $w_{++} - w_{+-}$, and it is shown to be plausible that if r

is large enough then "closure" of the new integral equation can be achieved by a less drastic assumption than superposition. This leads to an integro-differential equation that is valid at all r , but in which the direct potential does not appear. It is deduced from this relation among functionals of the potentials of average force that if κ is large, then $w_{ij}(r)$ exhibits damped spatial oscillations and implies a lattice structure extending over small distances. This apparently is achieved without invoking any attribute of the repulsive part of u_{ij}^* except (implicitly) its existence. Another novel approach to ionic interaction theory (23) considers the contribution U_e of the Coulomb forces to the potential by replacing $\exp(-U_e/kT)$ with an integral representation based on the theory of Gaussian integrals. The procedure is apparently valid at any κ , but an expression for the pressure of an ionic gas is obtained only at the low density limit.

Stillinger & Kirkwood (24) adapt the technique used in (22) to calculate the distribution of ions near a charged surface in the solution and conclude that above a certain concentration the ions distribute themselves in layers near the surface, with the spacing of the layers dependent on ion size and concentration. It is noteworthy that the calculated zeta potential has no kink at the transition concentration. Another calculation (25) for finite ion sizes, based on a modified Poisson-Boltzmann equation, has not led to a prediction of the layer structure. The screened interaction of two charged plates has also been investigated (26).

We turn now to the theory of transport processes. Helfand & Kirkwood (27) find that the limiting-law slope SQ^* for the heat of transport of an electrolyte comprises three terms: one for the mean ionic enthalpy; one for the long range forces; and a smaller term, only approximately evaluated, for the ion-solvent forces. A comparison of the calculated SQ^* with recent data (28) is satisfactory within the latitude allowed by the difficult measurements.

Compared to the Coulomb potential with cut-off, the direct potential introduced by Bogoliubov, $u_{ij}(r) = z_i z_j e^2 (1 - e^{-\kappa r}) / Dr$, is more convenient for many mathematical operations. From it, Kelbg (29) derives an analytical expression for $\Lambda - \Lambda_0$ including relaxation and electrophoretic terms. For $1/\alpha = 3.1\text{\AA}$ the calculated $\Lambda - \Lambda_0$ for NaCl(aq) agrees well with experiment up to 1M. It is instructive that a direct potential so different from that for the primitive model works at least as well by this criterion.

Fuoss (30) reinvestigates the equations for the velocity field to find that the Stokes' Law radius R and the distance of closest approach a are related by $a = R$ instead of $a = 2R$ as had previously been guessed. The effect on the calculation of $\Lambda - \Lambda_0$ is usually negligible.

EXCESS FUNCTIONS FOR STRONG ELECTROLYTES

The free energy data for solutions of strong electrolytes are customarily reduced by calculating activity or osmotic coefficients which correspond, respectively, to partial excess free energies of solute and solvent. The total excess Gibbs free energy per kg. of solvent,

$$G^{\text{ex}} = RTm[1 - \phi + \ln \gamma_{\pm}]$$

13.

is advantageous for some purposes (31). Here ϕ is the osmotic coefficient and m is the total molality of ions in the solution. This G^{ex} differs from the one in common use to characterize non-electrolyte solutions because of the essentially unsymmetrical character of the molality concentration scale used to define composition and standard states in electrolyte solutions.

For mixed electrolyte solutions it is natural to separate G^{ex} into two parts: the sum of G^{ex} for solutions of the component electrolytes all at the same ionic strength, and a quantity $\Delta_m G^{\text{ex}}$ pertaining to the process in which the component solutions are mixed at constant ionic strength I (31). For two electrolytes the equation

$$\Delta_m G^{\text{ex}} = RTI^2 y[1 - y]g_0$$

14.

is roughly equivalent to Harned's rule (y is the fraction of I due to one electrolyte and g_0 depends on T and I but not on y).

Harned (32) calculates a quantity equivalent to g_0 from data for a_{HCl} in HCl-KCl-H₂O. For 1M solutions, g_0 as a function of T has a maximum at 25°; this agrees with the calorimetric observation (33) that the quantity $h_0 = \Delta_m H^{\text{ex}}/RTI^2 y[1-y]$ is very small for the same systems. On the basis of Harned's rule and the Akerlof-Thomas rule, Iyengar (34) estimates heats of solution of salts in mixed electrolyte solutions from solubility data and obtains results consistent with the fragmentary calorimetric data. The systems, HCl-CdCl₂-H₂O and HCl-ThCl₄-H₂O at 25°, deviate markedly from Harned's rule (35, 36). In HCl-paratoluenesulfonic acid-H₂O at 25° Harned's rule is nearly obeyed at 1M (37) but there are deviations that increase with I . A technique different from the usual emf and isopiestic methods of investigating electrolyte mixtures allows the determination of both $a_{\text{H}_2\text{O}}$ and a_{HCl} by transpiration in HCl-MnCl₂-H₂O at 25° with I from 4.7 to 15 molal (38). Although the data are presented in a way that makes it difficult to calculate g_0 or compare activities at the same I , it appears that strong deviations from Harned's rule are found.

Curves representing the entropy of dilution of strong electrolytes as a function of I form a family, most of which can be generated in a simple way from a single curve if the crystal radii of the ions are used (39).

The osmotic coefficients of LaCl₃ solutions have been determined (40) by cryoscopy down to $3 \times 10^{-4}M$ and are found to fit a two-parameter Debye-Hückel equation with high precision. The effect on the parameters of including higher terms of the Gronwall-La Mer or Mayer theories is indicated. For aqueous LaCl₃, La(NO₃)₃, and NdCl₃ the heats of dilution (41) are fitted to an equation that is equivalent to $H^{\text{ex}}/I = A\Gamma^{1/2} + BI$, with the Debye-Hückel limiting law value for A , but an additional term in $I^{3/2}$ is required for ErCl₃, YbCl₃, and Yb(NO₃)₃. Some inconsistencies in the data and in comparison with theory are noted.

Isopiestic measurements (42) of aqueous CoEn₃(NO₃)₃, CoPn₃(ClO₄)₃, K₃Co(CN)₆, and (CoEn₃)₂(SO₄)₃ down to about 0.05M show that at a given

molality the first two have nearly the same γ_{\pm} while for the last, γ_{\pm} is similar to that for the more common 3-2 electrolytes. The activity of aqueous HCl from 25° to 250° has been determined by emf measurements (43, 44) and fitted to a Debye-Hückel equation at each temperature. It is found that \bar{a} is 4 ± 1 from 25° to 250° if data up to 1 *M* are fitted, but the resulting \bar{a} depends on *T* if only data up to 0.1 *M* are used. It is remarked that at high temperature the course of the γ_{\pm} curve resembles that in H₂O-dioxane of the same *DT* product. Isopiestic measurements at 100° lead (45) to osmotic coefficients for Li, K, Cs, and Ba chlorides and several sulfates from 1 to 4 molal. Most behave in nearly the same way as at 25°.

The equilibrium properties of aqueous solutions of one electrolyte and one nonelectrolyte are also described in terms of excess functions when it seems unreasonable to assume chemical interaction of the solutes. Then the data are reduced to Setschinow constants k_s . If, as usual, k_s is independent of electrolyte concentration, then k_s must consist of additive ionic contributions, but the data are not always consistent in this respect (46, 47). In the system alkali halide—tributyl phosphate-H₂O the solubility of nonelectrolyte is unusually low, 0.0016 molal, and the position of equilibrium is determined by counting radiophosphorous (46). However, the reduction of the data may be uncertain because some of the electrolytes are soluble enough in the (BuO)₃PO phase to change the chemical potential of the nonelectrolyte. For equal weights of dioxane and water as solvent and with naphthalene as nonelectrolyte, perchlorates salt out more strongly than chlorides, a reversal of the relation in water as solvent (47).

For ordinary systems the magnitude of $RTk_s \sim d\mu_0/dI$ is less than 0.3 kcal. mole⁻¹molal⁻¹ (μ_0 is the chemical potential of nonelectrolyte). The same is true for $d\Delta G/dI$ and $d\Delta H/dI$ for ionic reactions in solution unless there is a change of charge types in the reaction and *I* is low. However, Laidler *et al.* (48, 49) find that for the ionization of phenols or aryl ammonium ions in water ΔH is extraordinarily sensitive to ionic strength and in fact $d\Delta H/dI \sim 70$ –11 ΔH ranges from 33 to -11 in units of kcal. mole⁻¹molal⁻¹.

ION ASSOCIATION

We attempt to distinguish here between ion association, interpretable in terms of a model in which the ions are hard spheres with charges at their centers, and complex ion formation (next section) involving a more chemical interaction.

Howald (50) studies the position of equilibrium in the exchange of isotopic chlorine atoms between gaseous HCl and Cl⁻ in various forms in solution in pure acetic acid at 25°, with results expressed as the equilibrium constant for the reaction



The *K* values are HCl, 90; H₂OCl, 39; LiCl, 40; SrCl₂, 42; HgCl₂, 61. On the other hand, the values for HCl(g) and HgCl₂(g) are 46 and 70, respectively.

Because $K=40$ is expected (50) for Cl^- in a hydrogen-bonding environment the results support the widely held view that, in the ordinary concentration range, "ionophores" are disposed as solvent-separated ion pairs at moderate concentrations in polar solvents of low dielectric constant.

Pocker (51) studies the spectra of $\phi_3\text{CCl-Me}_4\text{NCl}$ mixtures in SO_2 . The $\phi_3\text{C}^+$ ion is yellow and the color is only partially suppressed by addition of Me_4NCl . On the assumption that two undissociated forms are present, colorless $\phi_3\text{CCl}$ and $\phi_3\text{C}^+\text{Cl}^-$ with the same spectrum as the free ion, he calculates the equilibrium constants for the formation of the ion pair and the complex from the ions. The calculated overall constant necessarily (52) agrees with the result from conductivity measurements. In solutions of iodides in sufficiently transparent solvents, ion pairing can be studied by its effect on the ultraviolet spectrum of I^- (53). Different effects are classified as attributable to contact ion pairs or to solvent-separated ion pairs. The association constants previously obtained by absorption spectroscopy for aqueous $(\text{NH}_3)_6\text{Co}^{+++}$ with Cl^- and Br^- are much too large (52). The absorption intensities of several bands of aqueous $\text{Pt}(\text{En})_3^{4+}$ are enhanced by SO_4^{2-} , Cl^- , Br^- , and NO_3^- , but not by ClO_4^- (54). The data are reduced to association constants which are found to decrease in the series of anions given. The interpretation is supported by the fact that at high anion concentration a saturation of the enhancement appears, although this does depend on the assumed equation for the activity coefficients.

The usual reduction of conductivity data leads to a parameter \bar{a} corresponding roughly to the distance of closest approach (in Angstrom units) of the centers of two ions. Fuoss uses the Fuoss-Onsager theory to calculate \bar{a} from a given set of data in as many as three independent ways (55 to 58) and finds a moderate consistency in the \bar{a} values. A more severe test of the physical meaning of \bar{a} may follow from additional observations more directly on ion pairs, e.g., from measurements of the dielectric constant of solutions (59). The reduction of the data involves a difficult correction [for a discussion see (60)] for the reaction fields caused by polarization of the solvent by the dipolar ion pair and then yields $\bar{a}=4.34$ for tetrabutyl ammonium picrate in benzene, compared to the range of values (4.67 to 6.64) from conductivity (61). It would be extremely interesting to make this comparison for $\text{Bu}_4\text{NB}\phi_4$ (57) for which the treatment of the conductivities is most successful.

Davies & Williams (62, 63) extend the measurement of the dielectric properties of these solutions to very high frequencies to investigate a process of energy absorption having a time constant of 10^{-9} to 10^{-10} sec. In most cases the process is orientation of ions in the electric field but there is also evidence for some field-induced dissociation of the ion pairs. The predominance of a single process for energy absorption over a range of concentrations is not consistent with some interpretations of the conductivity data that call for larger ion clusters at higher concentration. In calculating an \bar{a} parameter from these data (63), a correction different from that in (59) is used.

The explanation of the minimum in the curves of Λ vs. c for ionic solu-

tions in solvents of low dielectric constant, as given by Fuoss and Kraus in terms of ion triples, has been strongly challenged by Sukhotin (64). He points out that changing from single ions to triple ions as charge carriers implies an alteration in transport numbers, but for LiBr in a butanol-hexane mixture, in which c_{\min} is 0.01M, he finds $t_+ = 0.45$ at 0.002M and 0.46 at 0.1M. This can only be a coincidence from the point of view of the Fuoss-Kraus theory, but it is the expected result on the basis of a theory (65) indicating that the increase of c through c_{\min} results in a drastic lowering of γ_{\pm} for the free ions because of the increased ion concentration in the medium. This causes greater dissociation of the ion pairs. Measurements of dielectric constant (66) and activity coefficient (67) are cited in support.

We have here another example of the duality referred to in the opening paragraph of this review. For example, the formation of ion triples, $A^+ + AB \rightleftharpoons A_2B^+$, can be regarded as a chemical mechanism for explaining the sharp decrease of γ_{\pm} with increasing c , in the same way that ion pairing provides a chemical explanation of the low activity coefficients in dilute aqueous $CuSO_4$ solutions. It is exciting to speculate that the more physical theory (65) may lead naturally to the explanation of another common phenomenon in electrolyte solutions in solvents of low dielectric constant, namely, the coexistence of two liquid phases of different composition. This would result if $d\gamma_{\pm}/dc$ were negative enough in some range, and the solute in the dilute phase would be mostly ion pairs while the other would be mostly free ions.

Although nuclear magnetic resonance has been extremely helpful in investigating equilibria in which new chemical bonds are formed, its application to the study of ion-pair equilibria has yielded only rather vague results so far. Measurements of the F resonance (68) in a series of MF^{+n} ion pairs lead to a rough correlation between the resonance shift σ and the polarization, the latter defined as the ratio of the atomic number of the metal to the metal-fluorine distance. Valiev (69) discusses the theory of spin-lattice relaxation in these solutions. For the F resonance in a number of strong electrolyte solutions it is found (70) that σ depends on cations, anions, and solvent, while for the Cs resonance in such solutions σ is much less sensitive to solvent and other cations than to anions. In a study of the Na resonance (71), line widths and amplitudes rather than shifts are reported. For numerous sodium salts including the halides, nitrate and sulfate, the line width is independent of concentration and the amplitude is proportional to concentration up to $(Na^+) = 6M$. For others, including salts of amino acids, lactate, phosphates, and, most astonishingly, perchlorate, the line is wider and less intense than for "strong" electrolytes at the same concentration.

Metal ion—fluoride interactions seem to lie on the borderline between ion pairs and complexes (72, 73). For the fluoride complexes of Al^{+3} , the entropy changes (74) in the stepwise formation reactions after corrections for symmetry are given by $\Delta S^\circ = 15.8 - 2.9\Delta Z^2 \pm 1$ gibbs/mole where Z is the charge of the complex ion and ΔZ^2 applies to the stepwise reaction.³ George

³ 1 gibbs = 1 defined calorie/°K. See Giaque *et al.* (202).

(75) divides most ion-association reactions into two classes according to whether or not ΔS° for the association is linear in the hydration entropies of the ions. Class I includes complex ions (e.g. FeCl^{++}) but also $\text{Co}(\text{NH}_3)_4\text{Cl}^{++}$ (52) and CaHCO_3^+ , while MgSO_4 is typical of the ion pairs in class II, those for which ΔS° shows little dependence on hydration entropies.

It has long been believed that Ti^+ associates with negative ions more strongly than is expected for ion-pair formation. Creeth's study of the interaction with SO_4^{--} by an emf method is consistent with this (76). On the other hand, the Raman lines expected for the Ti-O vibration in $\text{TIOH}(\text{aq})$ and the closely similar $(\text{CH}_3)_2\text{TIOH}(\text{aq})$ evade detection although the corresponding line for $\text{CH}_3\text{HgOH}(\text{aq})$ is found (77). Moreover, positive evidence for the strictly ionic character of Ti^+X^- pairs is adduced from nuclear magnetic resonance investigations (78, 79).

Bruckenstein discusses the effect of ion pairing on the formulation of the acidity function H_0 in solvents of low dielectric constant (80). The stability of alkali halide ion pairs in ethylenediamine is investigated by an emf method (81) while conductimetric methods are used to study LiBr pairs in SO_2 (82) and the pairs $\text{Mg}^{++}\text{Cl}^-$ and CdCl^+Cl^- in ethanol (83).

Kay (84) applies the Fuoss-Onsager theory to reduce a large body of data for the conductivities of alkali halides in water, alcohols, and liquid ammonia. A single value of \bar{a} for each system enables one to represent the data over a wide concentration range. An amusing result is that \bar{a} —[sum of crystal radii] decreases from LiX to CsX , passing through zero at KX in H_2O and CH_3OH . The \bar{a} values for KX have previously been cited as evidence for the "physical" nature of \bar{a} in the new theory.

Spiro (85) demonstrates the ambiguity of conductimetric determinations of ion pairing in just those cases in which the "chemical" approach seems least reasonable. Conductimetric determinations of ion-pair association constants of $\text{LaCo}(\text{CN})_6$ and other electrolytes of this charge type in dioxane-water are reported (86, 87).

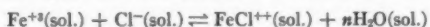
From ion-exchange equilibria it is deduced that the association of Fe^{++} and SO_4^{--} is measurably large (88). Similar small association constants are reported (89) for Cu^{++} , Co^{++} , and Ni^{++} with Cl^- and Br^- . In water above 300° ion pairing is much more extensive in NaOH than in NaCl (90).

COMPLEX IONS

Of the many interesting papers appearing in this field only a few can be mentioned here. This neglect is compensated by the recent appearance of a tabulation of dissociation constants of complex ions (91).

In ionic solutions an experimentally determined concentration ratio at equilibrium is usually much different from the thermodynamic equilibrium constant, but in favorable cases it is possible to work at low enough concentrations so that the thermodynamic constant can be determined by a short extrapolation (92). The sensitivity of association constants to the ionic medium is most vividly illustrated by Coll, Naumann & West (93) in a spectro-

photometric study of the $\text{Fe}^{+3}\text{Cl}^-$ interaction in aqueous HClO_4 . The results are conveniently expressed in terms of hypothetical 1M standard states for Fe^{+3} , Cl^- , and FeCl^{++} at each fixed acid concentration. Then the thermodynamic association constant K increases from 4.2 in 2.5M HClO_4 to 6100 in 9M. One might interpret these observations in terms of the reaction



with the extreme assumption that the states of the ions are independent of the medium. Indeed the observations are fitted by the equation $K = 1.5[a_{\text{H}_2\text{O}}]^{-8.86}$ implying $n \sim 9$. The association of CdCl^+ is also found to be sensitive to the ionic medium (94) and careful measurements of the activity of HCl in $\text{Ca}(\text{OH})_2$ - KCl mixtures fail to yield a precise dissociation constant for CaOH^+ because of difficulty in accounting for the medium effects (95).

An investigation of aqueous solutions by several techniques confirms that ReO_4^- is tetrahedral in solution while one form of silicate ion is identified as the structure $\text{SiO}_2(\text{OH})_2^-$, and in tellurates the tellurium has coordination number six (96). Much more elaborate structures are proposed by Muha & Vaughan (97) on the basis of x-ray diffraction studies of solutions of HfOCl_2 , HfOBr_2 , and the analogous Zr salts. An ion of composition $\text{Hf}_4\text{O}_{18}\text{Cl}_8$ (H omitted) gives a calculated intensity curve in good agreement with experiment for the HfOCl_2 solutions. Each Hf is surrounded by a square antiprism of eight oxygen atoms and is connected to each of two other Hf atoms by two O bridges. Each Cl atom is over 7Å away from the nearest Hf. The same structure is found in the other solutions; all are similar to the complex ions in the crystalline oxyhalide hydrates. Brady (98) interprets his x-ray diffraction study of ErCl_3 and ErBr_3 solutions with the help of the spectroscopic observations on aqueous Eu^{+++} solutions (99) which fix the symmetry around the ion as D_{2h} . The structure is determined to be $\text{Er}(\text{H}_2\text{O})_6(\text{H}_2\text{O})_3\text{X}_3^{++}$. Outer shell waters are included and two halide ions are located outside the first coordination shell. Comparison of calculated and experimental intensity curves unfortunately is not provided here nor does there seem to be a discussion in any of the x-ray studies of solutions about the possible effect of the approximation (100) necessary before one can Fourier-transform the intensity curve for mixtures.

Zaugg (101) interprets some kinetic effects in benzene solution in terms of the formation of complexes with Na^+ by molecules with large π moments.

ION SOLVATION

A reinvestigation (102) of the structure of liquid water by x-ray diffraction confirms the classical results of Morgan & Warren.

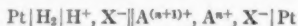
The nuclear resonance of O^{17} in water is not affected by diamagnetic ions but shifts to higher fields in the presence of paramagnetic ions. In mixed Co^{++} - Al^{+++} solutions, Jackson, Lemons & Taube (103) observe two O^{17} resonance peaks, one at the field characteristic of pure water and the other characteristic of aqueous Co^{++} solutions. Paramagnetic ions can affect only

those water molecules with which they come in close contact; this includes all of the solvent water that exchanges rapidly with water in the first coordination layer of Co^{++} . Therefore, the experiment shows that Al^{+++} holds back some water from the exchange process. It is found that water coordinated to Al^{+++} , Be^{++} , or Ga^{+++} does not exchange with the solvent within 10^{-4} sec., but water bound to H^+ , Li^+ , Mg^{++} , Hg^{++} , or Bi^{+++} exchanges more rapidly. An isotopic dilution study of $\text{Al}^{+3}(\text{aq})$ shows that there are 6 ± 0.4 H_2O molecules per Al^{+3} with half-times for exchange larger than 0.02 sec. (104). On the other hand, the proton resonances in aqueous $\text{HNO}_3\text{-Al}(\text{NO}_3)_3$ mixtures are used to count the "free" water molecules and nitrate ions (105); the hydration number of Al^{+++} by this measure is 10. Proton resonance in $\text{CrCl}_3(\text{aq})$ confirms the existence of slow solvation and other reactions in these solutions (106).

The electronic absorption spectrum of $\text{Mn}^{++}(\text{aq})$ is interpreted in terms of a field at the Mn nucleus due to six water molecules octahedrally arranged (107). The agreement with experiment is improved if the octahedron is slightly distorted. Rogers & Pake (108) confirm a new effect in spin resonance due to the structure around an ion, $\text{VO}^{++}(\text{aq})$ in this experiment.

Scherba & Sukhotin (109) find that ion—water interactions affect the infrared spectrum of dilute solutions of water in acetonitrile with added salts. A new band appears at 3470cm^{-1} when LiClO_4 , LiI , or $\text{Mg}(\text{ClO}_4)_2$ is added, but not $(\text{C}_5\text{H}_{11})_4\text{NI}$. The OH fundamental has also been observed in LiCl solutions (110) in undiluted methanol.

We now turn to thermodynamic aspects. The potential of the cell



serves as a measure of the solvation energy of H^+ , but of course also reflects the difference in solvation energies of $\text{A}^{(n+1)+}$ and A^{n+} . In order to obtain the dependence of the solvation energy of H^+ upon solvent by studying this cell in various solvents, one can use A ions of such a structure that the charge is well isolated from the solvent and then, with some confidence, apply the Born equation to calculate the solvent dependence of the half-cell on the right. Koepp, Wendt & Strehlow (111) use the ferrocene-ferrocinium couple on the right and, in each solvent, measure the potential over a range of compositions suitable for extrapolation to zero liquid junction potential. In this way they obtain the following values of the standard hydrogen electrode, relative to water, CH_3OH , 0.01v., CH_3CN , 0.15v., HCONH_2 , -0.15v. Practically identical values are obtained with a cobaltocene-cobalticinium reference electrode. Each of these potentials is the chemical part of the standard free energy of transfer (in electron volts) of H^+ from water to the other solvent. They are quite consistent with the values obtained from a very different method (111). It is deduced from a study of the cell $\text{Ag}|\text{Ag}^+, \text{NO}_3^-||\text{A}^{(n+1)+}, \text{A}^{n+}|\text{Pt}$ in $\text{H}_2\text{O-CH}_3\text{CN}$ mixed solvent, that in this mixture Ag^+ is preferentially solvated by CH_3CN . The ferrocene-ferrocinium and related couples used in this research have been the subject of a separate electrochemical study (112).

A similar method of dividing free energies into ionic contributions is used by Grunwald, Baughman & Kohnstam (113) with a very different experimental system, one that measures the composition of the vapor over solutions of electrolytes in 50 weight-per cent water-dioxane. Using estimated activity coefficients, the measurements lead to $k(s) \equiv d\mu^\circ(s)/dN_w$, the increase in standard potential of the solute with mole fraction of water in the mixture. It is proposed that $k(\phi_4\text{P}^+\text{B}\phi_4^-) = 2k(\phi_4\text{C}) + \text{Born charging term}$, and indeed this is experimentally verified with an accuracy of about 5 per cent. It is found that $k(\text{M}^+) = 15\text{kcal.}$ for $\phi_4\text{P}^+$, 7 for H^+ , and 0 to 3 for the alkali metal ions. But $k(\text{X}^-)$ is about -10 kcal. for the halide and several other negative ions. The results are most simply interpreted in terms of the preferential solvation of cations by dioxane and of anions by water. These $k(s)$ values seem very large compared to Setschinow constants (times RT) but this is merely due to a difference in concentration scales.

Another method of investigating single ion solvation energies proposed by Izmailov (114) is based on plots of the solvation energies of $\text{H}^+ + \frac{1}{2}[\text{X}^- - \text{M}^+] = \text{H}^+ + \text{X}^- - \frac{1}{2}[\text{M}^+ + \text{X}^-]$ as a function of $1/r$, where r is the mean radius of M^+ and X^- . Good extrapolations to $1/r=0$ are taken to establish the chemical solvation energy of H^+ . One result that can be compared with (111) is the standard potential of the hydrogen electrode in methanol relative to water: Izmailov gets 0.20 v.

The intense ultraviolet absorption of iodide ion and various iodide ion pairs is very sensitive to the nature of the solvent. The maximum is usually a doublet with splitting about 21.7 kcal./mole, the difference in energies of the $^2P_{3/2}$ and $^2P_{1/2}$ states of iodine atom; hence, in the excited state one electron has a low probability density in the iodine atom. The spectrum is sensitive to solvent because the more strongly the iodide ion is solvated in its ground state, the higher the energy of the transition, since the solvent dipoles are unable to adjust to the new position of the charge during the time of the transition. On this basis one can hope to learn about solvation energies by studying such spectra.

For the N-alkyl pyridinium iodide ion pairs Kosower *et al.* (115) compare the dependence of transition energy ("Z value") on solvent with other measures of solvent ionizing power. In the excited state the electron from the iodide ion is supposed to be on the pyridinium ion; however, the splitting of the doublet varies from 16 to 29 kcal./mole in various systems, suggesting a strong interaction with the I atom. Other studies focus on systems in which the electron from I^- is largely transferred to the solvent in the excited state (116 to 120). There is some disagreement about both the theoretical interpretation and the observations, many of which relate to fine details such as temperature and salt effects. Regarding the theory, Smith & Symons (121) attribute the medium sensitivity mainly to the excited state, Stein & Treinen (116) mainly to the ground state, while Kosower, for his slightly different system, gets equal contributions from both. It seems worth noting that the latter two theories have thermodynamic corollaries. For instance, the difference in Z values of H_2O and CH_3CN (namely, 24 kcal./mole) implies that the

ΔH of transfer of an alkyl pyridinium iodide from H_2O to CH_3CN is 12 kcal., which is to be compared with the small difference in solvation free energy of protons in these solvents (111). In a similar way Stein and Treinen's theory leads to definite conclusions about the partial molal heat capacity and partial excess enthalpy of I^- ; this aspect invites further study. Another promising system for the study of spectra of this sort is PdX_4^{2-} , which interacts with the solvent in the fifth and sixth coordination positions (122).

An extension of Kosower's Z -value measure of solvent ionizing power is proposed by Brownstein (123) in the form

$$f_{soln} - f_{EIOH} = Tsr$$

where: depending on the application, f is ΔF^\ddagger of a kinetic process, or ΔG° of an equilibrium process, or $h\nu$ of a spectroscopic transition; T is the temperature; s a parameter characteristic of the solvent; and r a parameter characteristic of the kinetic, equilibrium, or spectroscopic process. The application of the scheme to a variety of processes in dozens of solvents and hundreds of solvent mixtures supports the empirical validity of these correlations.

Theoretical considerations of solvation numbers are made on the basis of a model with a field-strength-dependent dielectric constant for the solvent (124), and on the basis of the kinetics of the exchange of water between the solvation layer and the bulk solvent (125, 126). More qualitative discussions of ionic solvation are based on free-energy data for aqueous solutions (127), heats and free energies (128), and viscosities (129 to 131). Perhaps the simplest solvation quantity to understand is the entropy change but, by considering a wide range of data, King (132) finds that $\Delta S_{hydration}$ does not have the simple power dependence on either the ionic charge or the crystal radii that one expects from the several models that have been proposed.

The equilibrium distribution of an electrolyte between two different solvents is closely related to the difference of solvation energies of the ions in these solvents and may be used in the investigation of the solvation energies except for the prevalence of complications, the most noxious of which is lack of knowledge of the electrolyte species in each phase.

In the extraction of $In(III)$ from aqueous HCl by organic solvents, the electrolyte species in the organic phase is, in addition to some form of HCl , presumably the solvated proton- $InCl_4^-$ ion pair (133). For the same system Irving & Lewis (134) calculate the dependence of partition coefficient on solvent in terms of three contributions to the solvation energy of the ions (Born charging, short-range ion-solvent interaction, and energy of cavity in solvent) and, in addition, a calculated ion-pairing constant. The theory is remarkably successful in correlating the data for a variety of solvents, mostly mixtures of methyl isobutyl ketone with another component.

The extraction of $Fe(III)$ from HCl solution into C_6H_6 or $CHCl_3$ is enhanced by various amines (135). As a first step in interpretation it is shown that the iron species in the organic phase is $RNH_3^+FeCl_4^-$. For preparative purposes one of the most useful extractants is tributyl phosphate. The phase

in equilibrium with dilute and aqueous solution closely approximates $(\text{BuO})_3\text{PO} \cdot \text{H}_2\text{O}$ in composition. Hesford & McKay (136) find that in this phase HClO_4 is a strong acid, while for HCl , H_2SO_4 , and HNO_3 , $K_a \sim 10^{-4}$. Especially impressive is the demonstration that the concentration dependence of the HClO_4 partition conforms to the Debye-Hückel limiting law over a measurable range. It is surprising then to find that a number of alkali halides behave like weak electrolytes in $(\text{BuO})_3\text{PO} \cdot \text{H}_2\text{O}$ (137).

TRANSPORT PROCESSES

In mixtures of two electrolyte solutions of the same ionic strength the ionic conductances λ_i vary with the mixing fraction y . Kell & Gordon (138) find that for aqueous 0.01 M LiCl-KCl , $d\ln\lambda_i/dy = 0.013$ for K^+ and 0.020 for Li^+ ($y=1$ for KCl). This is to be compared with $d\ln\lambda_i/dy = 0.0046$ for each ion calculated from the limiting ionic interaction theory of Onsager and Fuoss.

Other systems having new or refined conductance measurements include: aqueous solutions of sodium hexanoate (139); LiF (140); $\text{KAg}(\text{CN})_2$ (141); MAsF_6 (142); $\text{M}^{\text{I}}_2\text{M}^{\text{IV}}\text{F}_6$ (143); $(\text{Me}_4\text{N})_4\text{Mo}(\text{CN})_8$, $\text{K}_4\text{W}(\text{CN})_8$, and $\text{K}_2\text{Pt}(\text{CN})_4$ (144); and ZnSO_4 and $\text{Zn}(\text{ClO}_4)_2$ (145). Kilpatrick interprets the composition dependence of proton conductance in $\text{H}_2\text{O-H}_2\text{O}_2$ and $\text{H}_2\text{O-CH}_3\text{OH}$ in structural terms (146). An improved value of t_+ is reported for $\text{H}_3\text{PO}_4(\text{aq})$ (147).

The isotope dependence of the electromigration of Li^+ in agar gel implies a hydration number of 46 if one makes the usual assumption that the mobility is inversely proportional to the square root of the mass (148). This hydration number does not compare well with the value of 20 as deduced from an earlier isotopic mobility study in water (149).

Since the relative motions of cations and anions are different in conduction and in diffusion, the cross coefficients L_{12} of the linear phenomenological theory enter the two processes in different ways. Miller (150) solves for L_{+-} in terms of the conductivity and diffusion coefficients and calculates L_{+-} from the data for several salts. An empirical limiting law is found for L_{+-} .

Both experimental and theoretical aspects of diffusion in three component systems receive attention (151 to 154). The Onsager reciprocal relations in one such system are verified within 8 per cent (155). The phenomenological theory of diffusion in solutions of weak electrolytes is worked out (156, 157) and applied with success to $\text{Ti}_2\text{SO}_4(\text{aq})$ (158).

Mills *et al.* find that at low ionic strength the diffusion of an alkali metal ion or halide ion, present at trace levels, is retarded in conformity with the Onsager limiting law (159), but at higher I the retardation depends on the ionic medium in a way that indicates a specific interaction of like-charged ions (160, 161). Such effects are even larger in the trace diffusion of H^+ (162). Berne & Weill find that the early measurements on the self diffusion of I^- in $\text{NaI}(\text{aq})$ are in error (163) and that the self diffusion of I^- in AgI-I^- solutions is consistent with the existence of polynuclear complexes such as $\text{Ag}_4\text{I}_6^{4-}$ in

the solutions (164). It is found that the diffusion of KCl in H_2O -glycerol is difficult to measure accurately enough for comparison with the Onsager-Fuoss theory (165).

Mobilities of aqueous nonelectrolytes are of interest for comparison with ionic mobilities. The sedimentation velocity of $\text{OsO}_4(\text{aq})$ corresponds to a Stokes' Law radius of 2.1 Å, in agreement with a radius of 2.2 Å as estimated from electron diffraction data (166).

Toor (167) derives the equations for the diaphragm cell with improved generality. Experimental aspects have also been discussed for the investigation of diffusion by conductance (168), ultracentrifugation (169), and chemical kinetics (170).

DeBethune gives a pedagogically useful systematization and review of the application of the Onsager reciprocal relations to electrochemical systems with a temperature gradient (171). The relations of the heat of transfer to the Soret coefficient (172) and to a calorimetrically determinable quantity (173) are discussed, as is the rate of attainment of Soret equilibrium (174). Snowden & Turner (175) give an extensive tabulation of directly determined Soret coefficients in 0.01*N* aqueous salt solution. These coefficients are closely additive in the ions and are in accord with data from thermocells.

The theory of electrodifusion, the cross effect between charge transport and diffusion in ionic systems, is further elaborated (176, 177). This effect, as yet unexploited, depends on the random changes in mobility that some species undergo as a result of chemical reactivity and it may be useful for investigating some fast reactions.

NONAQUEOUS SOLUTIONS

Laboratory technique.—Several ways to reduce the increment of difficulty usually found in making a given physicochemical measurement in anhydrous solutions rather than in wet have been reported. One example is a procedure for electrochemically generating anhydrous HClO_4 in CH_3CN (178). Another is a technique of coulometric Karl Fischer titration in MeOH (179). A new apparatus for conductivity measurements with rigorous exclusion of water is demonstrated with measurements on SnI_4 using several solvents (180). Most promising are Félici's applications of ion exchange resins to reduce the specific conductivity of solvents to intrinsic values (181, 182). Thus, the resistivity of EtOH is found to be 43.3×10^9 ohm cm. compared to a value 44.7×10^9 calculated from the self-dissociation constant derived from emf measurements. A procedure for solubility determinations by conductivity gives precise results without chemical analysis of the liquid phase (183).

Liquid ammonia.—From their calorimetric heats of solution of solid salts, Gunn & Green (184) find that below 0.04*M* the heats of dilution to 0.003*M* are the same within experimental error for the following salts: NH_4I , KI , CsI , NaCl , and $\text{Ba}(\text{NO}_3)_2$. For KI , from 0.4 to 5 *mM*, the \sqrt{c} slope is 27 kcal. mole^{-3/2} l^{-1/2} compared to the limiting law slope of 2.3 in the same units. The role of ion-pairing is enigmatic here. It both levels the heats of dilution and,

in the lower concentration range, preserves the proportionality to the square-root of concentration. Accurate solubility measurements of the alkali halides, including analyses of the solid phases in equilibrium with the solutions, are reported for the temperature range -80° to -34° ; a thermodynamic treatment of the data has not yet been made (185).

Dye, Sankauer & Smith (186) use the moving boundary method to re-determine the transport numbers in Na solutions from 0.02 to 0.15 *M*. The new t_+ values are combined with conductivity data to get λ_+ in the solutions and the deviation of this λ_+ from the limiting law is used as a basis for calculating equilibrium constants for the reactions



The cation conductance λ_+ is preferred to the total equivalent conductance Λ for this purpose because of the possible contribution of metallic conductance to λ_- , even at concentrations as low as 0.15 *M*. However, the constants $K_1 = 9.2 \times 10^{-3}$ and $K_2 = 18.5$ are in good agreement with those (7.2×10^{-3} and 27) calculated from Λ . The same transport numbers (186) applied to old emf data for cells with transference yield new values of the stoichiometric γ_{\pm} for Na solutions (187). These are consistent with the constants K_1 and K_2 determined in (186) combined with a Debye-Hückel equation, including ion size, for the free ions. It is deduced (187) that S°_{-33} for $e^-(\text{NH}_3)$ is 17 ± 2 gibbs/mole [relative to zero for the standard entropy of $\text{H}^+(\text{NH}_3)$], which is to be compared with 2 gibbs/mole from Latimer & Jolly (188) for $\frac{1}{2}e_2^-(\text{NH}_3)$ and with 40 from Dewald & Lepoutre (189) using Latimer and Jolly's value for the absolute entropy of $\text{H}^+(\text{NH}_3)$. New observations of the spectra of Na and K solutions at -65° show that the band at 1480 $m\mu$ has the same shape for both metals over a range of concentrations (190). This band is generally believed to be characteristic of $e^-(\text{NH}_3)$ while that at 670 $m\mu$ is attributed to the dimer Na_2 or K_2 . The meaning of the spectral data for a model involving four solute species, e^- , M^+ , M , and M_2 , is reviewed by Evers (191). Perhaps some of the remaining uncertainty could be dispelled by magnetic and spectroscopic studies of mixtures of metals and metal halides in liquid ammonia as well as of solutions of $(\text{C}_4\text{H}_9)_4\text{N}^+e^-$ (192). Such data might also provide a basis for interpreting the thermocell data (189) in a way consistent with the low value for the entropy of $e^-(\text{NH}_3)$.

Conductivity studies of the closely similar solutions of Li in CH_3NH_2 lead to $K_1 = 5.8 \times 10^{-3}$ and $K_2 = 5.4$ for the reactions in this system analogous to chemical equations 15 and 16 (193, 194).

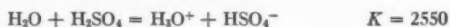
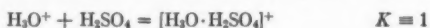
Sulfuric acid.—By studies of proton resonance in sulfuric acid solutions, Gillespie & White (195) show that HSO_3F and HSO_3Cl are weak acids in this medium while $\text{HB}(\text{HSO}_4)_4$ is moderately strong. Conductimetric titrations are used to determine the basicities of several aryl-nitro compounds (196). A Debye-Hückel equation, limiting law plus a linear term, is found to fit the

osmotic coefficients derived from cryoscopic measurements on solutions of $\text{H}_2\text{S}_2\text{O}_7$, $\phi_2\text{CO} \cdot \text{H}_2\text{SO}_4$, and the bisulfates of Li, Na, K, Ag, and Ba (197). The long range interaction effects here are relatively unimportant because of the high dielectric constant and high ionic strength of this solvent. Limiting partial molar volumes have also been determined (198).

The high mobilities of lyonium and lyate ions imply a chain mechanism for proton transport in H_2SO_4 , so it is intriguing that Greenwood & Thompson find the activation energy for conduction to be the same in H_2SO_4 and D_2SO_4 (199).

Walfaren & Young (200) conclude from a Raman study of H_2SO_4 - SO_3 mixtures that the concentration of the species H_2SO_4 decreases while $\text{H}_2\text{S}_2\text{O}_7$ and HS_2O_7^- increase to a maximum as the stoichiometric mole fraction N_2 of SO_3 approaches 0.55. There is a maximum in specific conductance at $N_2=0.2$. In all these mixtures the predominant anion is HS_2O_7^- rather than HSO_4^- . In media characterized by $N_2=0.65$ the conductivity behavior of several electrolytes is similar to that in H_2SO_4 (201).

Giauque *et al.* (202) review their extensive researches on the thermodynamic properties of H_2SO_4 - H_2O solutions and crystalline compounds. Wyatt (203) assumes the equilibria



and also assigns ΔH° and ΔV° values. With the additional assumption that these species mix ideally he is able to calculate values of H_0 , water activity, partial molal enthalpy of water, and density for H_2O - H_2SO_4 solutions (in the range 80 to 100 weight per cent H_2SO_4) with excellent agreement with the observations. This appears to be a triumph of the chemical approach.

Miscellaneous solvents.—In the system H_2O - P_4O_{10} there is no minimum in conductance at the composition H_3PO_4 (204). In pure H_3PO_4 the ion H_2PO_4^- has a very high mobility, implying the operation of a chain transport mechanism for H^+ . Greenwood & Thompson also find evidence that $\text{BF}_3 \cdot \text{H}_3\text{PO}_4$ is an ionic liquid at room temperature, presumably $(\text{HO})_4\text{P}^+ \text{P}(\text{OH})_2(\text{OBF}_2)_2^-$ (205).

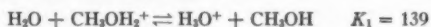
Dissociation constants for HCl , H_2SO_4 , and HClO_4 in pure acetic acid obtained by emf methods are found to be several units lower than older results (206). Waddington & Klanberg (207, 208) find that liquid HCl solutions of Me_4NCl and BCl_3 react to form a solution of Me_4NBCl_4 from which the solute can be obtained in crystalline form. Like Me_4NCl , PCl_5 acts as a base in this solvent and can be used to titrate solutions of the acid BF_3 to obtain a solution of $\text{PCl}_4^+ \text{BF}_2\text{Cl}^-$ from which the solute can be crystallized. The BCl_4^- ion is also formed when SO_2 solutions of BCl_3 are mixed with $\text{KCl}(\text{c})$ (209).

Tetramethylene sulfone is proposed as a medium for strongly basic

reagents. An H_- value of 20 has been established for solutions of $\phi\text{Me}_3\text{NOH}$ in this solvent (210). Trimble (211) finds that the alkali chlorides and several other salts are reasonably soluble in 2-methoxyethanol. The solubility of KCl is 0.057 molal, that of KClO_4 is greater.

A spectroscopic investigation of Fe^{III} in N-methyl acetamide shows the acidity of the ion to be about the same as in water while its Cl^- affinity is much larger (212). The properties of the mixed solvents, N-methyl acetamide and dimethyl formamide and the conductivities of solutions of NaBr, KBr, and KI in the mixtures are determined by Dawson & Wharton (213). For amine bases in acetonitrile an analogue of Pitzer's rule for the entropy of ionization of aqueous acids is found to apply (214). For aniline derivatives ΔH of ionization correlates with Hammett σ values.

The standard potential of the Ag/AgBr electrode is redetermined in pure MeOH by measurements down to 0.0005 M and found to be -0.1375 v. (215). Strehlow (216) shows that data for Λ_0 of HCl in MeOH with 0 to 15 mole per cent water are accurately fitted by calculations from a chemical model in which the added water reacts according to



with mobilities of the ions independent of composition in this range. The value of K_1 is in good agreement with an emf determination. A similar procedure applied to EtOH solutions yields $K_1' = 250$; the results considered together imply that $H_0(\text{MeOH}) - H_0(\text{EtOH}) = 0.25$ when water is the indicator. This is in poor agreement with the difference 0.14 obtained for aniline as the indicator.

Janz & Danyluk (217) review the data on conductivities of hydrogen halides in polar organic solvents and reduce the data to Λ_0 and K values. The solubilities of Cs_2SO_4 in several alcohols (218) and of AgCl and CsCl in several alcohols and ketones (219) fit an equation of the form, $\log(\text{solubility}) = a + b/D$, where a and b are characteristic of the salt and D is the solvent dielectric constant.

Fraser & Dasent (220) report a detailed study of the complexes of cupric halides in EtOH, CH_3CN , HCO_2H , and H_2SO_4 . Under some circumstances the reaction $\text{CuBr}_2 + \text{NO} \rightleftharpoons \text{CuBr} + \text{NOBr}$ occurs.

MISCELLANEOUS AQUEOUS SOLUTIONS

Most acidity studies have been omitted from this review, but of outstanding interest are the results of Hood & Reilly (221) for the thermodynamics of dissociation of HNO_3 and HClO_4 deduced from proton magnetic resonance experiments at three temperatures. To reduce the data it is assumed that there are just three protonic species in each solution: H_2O , H_3O^+ , and the undissociated acid. For HNO_3 , K_d is 28, for HClO_4 it is only 48. Even more surprising are the ΔS° values for acid ionization, -5 and $+1$ gibbs/mole respectively, compared to Pitzer's rule which gives -20 . Apparently most of the ability of the proton to polarize the solvent is retained

in the "undissociated acid" species identified by the proton resonance study. Proton resonance, Raman, and classical methods all give $K_d = 0.18$ for HIO_3 (222).

We close with a report of great novelty. Trumpy (223) describes some features of the chemistry of positrons and the species positronium (positron chemically bound to electron) in water. For the most part it is difficult to distinguish between equilibrium and kinetic effects but it is strongly indicated that the oxidation potential of positronium is near zero.

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SOLUTIONS OF NONELECTROLYTES¹

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Efforts in the field of solutions during the past year could perhaps best be characterized as being on the whole destructive of previously used notions and concepts. At least this is what struck the reviewer when reading the many articles published in this area. It is, of course, from such critical tests of accepted generalizations that new generalizations, usually of a more specialized kind, evolve. This latter process is forced upon the description of solutions by the increasing accuracy of experiments.

On the experimental side, the outstanding event during the year was a discussion concerning the effect of environment upon molecular energy levels, under the leadership of H. W. Thompson. This discussion shows that the study of solutions by the various spectroscopic methods can provide valuable and detailed information about the state of a molecule in solution. This experimental and theoretical effort is just starting and is occasioned mostly by the higher resolutions of the instruments now available. A more extensive than usual description of this activity is hence included in this review.

On the theoretical side, the outstanding event during the year was a meeting honoring the late Professor J. G. Kirkwood. The many papers presented at the symposium, covering the numerous aspects of Chemical Physics which he stimulated, show again, if proof is still necessary, his immense and lasting contribution to science. The fact that his efforts in the area of solutions and liquids have not yet led to a good quantitative theory for even the simplest condensed systems is hardly a blemish on his record, but rather a testimony to the difficulty of the problem. It is only during this year that his various theories about liquids have come to a serious quantitative test. It will now be necessary either to carry his theories to a higher approximation or to develop a new initial approximation. Although both of these approaches have begun within the last few years, the latter procedure appears the easier. However, it is not clear whether these theories will be an improvement. Quantitative tests should be forthcoming during the next few years.

Another important event during the year has been the translation of more Russian journals into English. Of particular value is the transcription of the *Russian Journal of Physical Chemistry*, which contains many articles on solutions. Since the Russian contributions to this field have not been extensively covered during the last few reviews, and since from now on it should be easier to keep us aware of their work, a fairly extensive survey was made of titles of articles appearing in the major Russian journals over the last few years, as covered in the "Library of Congress—Russian Accessions List." Only about half of the more interesting sounding titles could be read in

¹ The survey of literature pertaining to this review was concluded in December 1960.

English in either abstract form or complete translation. It would have been particularly desirable to have available a translation of the *Ukrainian Journal of Physical Chemistry*. In spite of these handicaps, a fair picture of the state of affairs has been obtained. The Russian investigation into all aspects of phase diagrams of a great variety of systems represents a particularly strong effort. Of the several hundred such articles found, only those of a general nature or particular interest have been included here. The same statement can be made about the study of complexes. Experimental x-ray studies of liquid metallic mixtures are represented by a number of articles.

The problem of describing all the properties of a solution from a molecular point of view can be divided into two parts. The first part concerns the knowledge of the interaction potential between all the particles, and the second part is the derivation, by means of statistical mechanics from this interaction potential, of the equilibrium properties from the partition function, and of the non-equilibrium properties from the Liouville equation. Progress in each of these areas will be taken up in turn, but more emphasis has been placed on the knowledge of the potential than usual. Unfortunately, this has necessitated a shorter discussion on the thermodynamic aspects of liquid mixtures.

THE PAIR POTENTIAL

The total potential of interaction between the particles of a condensed system has almost universally been written as pair-wise additive for chemically saturated molecules. It will be shown in the next section that what constitutes chemically saturated molecules, especially when two molecules of two different species interact, will have to be radically revised in view of experimental results on complexes. Nevertheless, the total potential can always be written as pair-wise additive if the system is dilute so that binary encounters are the only significant events. To be safe, then, knowledge of the pair potential can be obtained only from thermodynamic, transport, and spectroscopic measurements at low density or from molecular beam scattering experiments.

LONG RANGE PART

The state of the theoretical knowledge of the pair potential has been summarized recently by Pitzer (1) for the long range behavior. The London theory predicts that the potential falls off as the inverse 6th power of the distance between the particles; however, the theoretical numerical coefficient of this attractive term is as much as 50 per cent lower than the experimental values for the heavier molecules. The Slater-Kirkwood formula, on the other hand, gives too high a value. Pitzer points out that these quantum mechanical calculations must be made more exact by considering the effect of the inner electrons of an atom and by considering correlation terms rather than the one-electron wave function approximations. For the very light elements these effects are reduced, and hence theory and experiments agree within a few percentage points. Salem (2) follows Pitzer's suggestion and includes two electron correlation terms by second order perturbation theory and

furthermore utilizes the experimental magnetic susceptibility in the expression for the polarizability, as does the Slater-Kirkwood formula. These improvements bring the theoretical values for the attractive constant to the high side of the experimental value but closer than before. For the theoretically favorable case of the argon-helium interaction, the calculation is within the apparently large experimental uncertainty of the dispersion constant (20 per cent) and differs by 10 per cent from the frequently used geometric mean of the dispersion constants of pure argon and helium.

Experimental evidence that the potential at large separation falls off as predicted by the London theory has been rather indirect up to now. It has come mainly from fitting properties at low density with expressions involving certain integrals of the potential of interaction. This procedure certainly does not uniquely determine the form of the potential, since only if the potential were monotonic could it be uniquely determined. However, the fact that many properties involving different integrals yield approximately the same value for the attractive coefficient gives reasonable confidence in the theory, and the fact that the coefficient for the light elements agrees with the theoretical value is also an aid. In addition, a series of very careful and ingenious experiments have recently yielded the desired direct measurement of the molecular attraction and, furthermore, have shown the correctness of the so-called retarded effect.

The retarded effect arises from the notion that the London dispersion theory is valid only so long as the distance separating the particles is small compared to the wavelength of a typical electronic transition of the atom and, of course, large compared to the dimension of the atom. When the distance between atoms is large compared to the wavelength of the atomic transition, the potential falls as the inverse 7th power of the distance because of the finite time of the transmission of electromagnetic waves, hence the term, "retarded." Thus, the potential can be deduced by measuring the extremely small force between two macroscopic solid objects held extremely close together. The results of the Dutch (3) and Russian groups (4, 5) are now in complete agreement. The exponent of the power law found empirically to fit the data is within 5 per cent of the theoretical exponent, and the dispersion constants for the fused quartz used in the experiment seem to agree within 10 per cent. Moreover, when the objects were brought very close together (50 Å) the retardation effect disappeared. These experiments have been criticized (6) because they involve condensed bodies, and hence the many-body aspect of the problem has to be considered. Although it is true that this effect makes the interpretation of the dispersion constant difficult, it will not invalidate the power law dependence of the potential since the leading term at large distances is evaluated by the London theory.

MOLECULAR BEAMS

Knowledge of the potential when two particles are close together is much less certain. This is because it is necessary to solve the very difficult many-electron problem when the electron clouds of the atoms overlap. The Thomas-

Fermi model of the atom (7) can usefully be employed when the atoms are extremely close together. The experimental information comes most directly from the cross section in molecular beam experiments. Depending on the energy of the beam, different regions of the potential are emphasized. The situation in this area can perhaps be summarized best by saying that, in the very repulsive region of the potential, theory and experiments disagree by at least a factor of two in the simplest possible situation, that of helium. This year only two examples of these valuable and difficult beam experiments were found in the literature. Both of these are concerned with thermal beams and hence emphasize the dispersion term. The scattering of potassium and cesium from various simple gases (8) shows that the cross section differs by a constant value (about 50 per cent) from the theoretical value based on the London dispersion theory, but relative values of the cross section can be predicted within a few percentage points. Using cesium chloride instead of cesium (9), the same situation is again encountered for non-polar gases, but for polar gases the relative agreement is considerably worse, mainly because the angular dependence of the dipole-dipole interaction potential was not properly taken into account.

SECOND VIRIAL COEFFICIENTS OF PURE SYSTEMS

The repulsive potential is always very steep and is usually represented as an exponential or a high inverse power of the distance. Unless very high temperature macroscopic data are available, it is possible to fit low density data equally well with various functional forms of the repulsive potential. The high temperature, thermal conductivity measurements on helium and hydrogen (10), for example, show that these repulsive forms fit the data badly; the potential derived from molecular beams is more satisfactory. However, by combining any such repulsive potential with the inverse 6th power attractive potential, most of the low density data can be reproduced within experimental accuracy. For the second virial coefficient, for example, this is shown for helium (11) and for the transport coefficients for krypton (12). Krypton is interesting because the potential obtained from transport data does not fit the second virial data well, regardless of which repulsive form is used. The two parameters involved in the potential for the virial data are significantly different. In general, however, unless the low density data are very precise and extensive, the information available allows the determination of only one constant of the two-constant potential; that is, within reasonable limits there is a set of the pair of constants which yields agreement with experiment.

The fact that the second virial coefficient is insensitive to the potential is again emphasized in a report by Boys & Shavitt (13). They propose the following very sensible mathematical procedure: that the potential, $U(r)$, be expanded systematically by means of a linear combination of a set of complete functions.

$$U(r) = \frac{4\epsilon}{(r^3 + B^3)^3} \sum_{i=0}^{\infty} C_{2i} [r^{2i} e^{A(1-r^3)} - 1],$$

where r is the reduced distance between particles, the parameters A and B are fixed so as to give a qualitative fit to the potential, and as many linear coefficients C_{2i} are used as necessary to fit the data. ϵ is just a scaling factor for the C_{2i} constants. Various choices of C_0 , C_2 , and C_4 led to the same second virial coefficient but to rather different potentials. On the other hand, the third and fourth virial coefficients could more accurately determine C_0 , C_2 , and C_4 if good data were available at low temperatures. The choice of Gaussian functions is mathematically convenient, basically because it is possible to carry out a many-dimensional integration with them. Thus it was possible to evaluate for the first time the fourth virial coefficient for a realistic potential (14).

Although the third and fourth virial coefficients could contain effects attributable to the non-additivity of the potential, in any case they are not accurately enough known to determine the potential more precisely. Michels (15, 16), who has taken some of the most accurate virial data, points out that the experimental error in the second virial coefficient is only a few tenths of 1 per cent, the error in the third is around 15 per cent and in the fourth around 100 per cent. The precision of the second virial data might hopefully be still further improved by utilizing an experimental technique (17) which requires only the measurements of volume changes.

Some of the second virial data are accurate enough to show that a two-parameter potential is inadequate. It would be surprising if the potential were to be very realistic at intermediate distances near the minimum when the asymptotic forms, valid at large and small distances, are arbitrarily combined. One difficulty is that the higher order terms in the London dispersion theory become significant at these intermediate distances. From lack of any information to the contrary it will be assumed, in order to judge their effect on the pair potential, that these higher terms form a geometric series. Thus, the attractive term for distances R several times R_0 can be roughly represented as proportional to

$$\frac{1}{R^6 \left[1 - \left(\frac{R_0}{R} \right)^2 \right]},$$

where R_0 is of the order of the dimension of a molecule. The effect of such a term is to make the bowl of the potential steeper, that is, to make it look more like a square-well potential.

There are, however, further complications when the interaction of two equal molecules, rather than atoms, is considered. For example, for non-polar diatomic molecules, the anisotropy of the polarizability has to be taken into account as well as the angle dependent repulsive interaction. For hydrogen and deuterium it was not possible to fit the second virial coefficient (16) with a two-parameter potential, even though these effects were allowed for and quantum corrections included. One reason for this could be that the angular aspects were inadequately treated; however, the form of the spherically symmetric part of the potential for hydrogen could be quite different

from that for a rare gas atom because the electrons are mostly confined to the interior of the molecule. We shall return to this point later.

When the interacting molecules are polyatomic, as with large hydrocarbons, it becomes necessary to consider that the interactions of the atoms on the surface of the molecules are the most significant (18) for all but very large separation distances, and the previous two-parameter potential forms no longer give the correct temperature dependence of the virial coefficients. The Kihara potential is then a better approximation. This potential adds a third parameter, which represents the core size of the molecule, and interaction distances between the molecules are then measured from the core. This has the effect of steepening the repulsive part of the potential. It might be added that such an effect should also exist to a smaller extent even in the interaction between rare gas atoms. After all, it is the interaction between the outer electrons of an atom which makes the major contribution to the potential. For example, xenon should have a slightly steeper repulsive interaction than argon.

Before going into the additional complications introduced in the interaction between unlike molecules it is worth-while to show that similar complications can occur in pure systems. At low temperatures and low densities it can be useful to consider the system as a mixture of bound, metastable, and free molecules (19). At high temperatures the interaction of differently excited, like atoms has to be calculated (20). For odd-electron atoms at large distances, valence forces predominate over dispersion forces and change the power law of the interaction. For transport properties at high temperature (21), similarly, different interaction energy curves, resonant excitation, and charge exchange must be considered. Again, for transport properties it is useful to consider dimers in explaining the initial pressure dependence (22). However, the equivalent expansion to the virial series for the transport properties has not been as thoroughly investigated experimentally. Since the coefficient of the second power of the density for the various transport properties should soon be numerically evaluated, experimental interest in this coefficient should increase. In this connection, a density expansion of the viscosity (23) in reduced form was successfully executed for a number of simple gases. The temperature dependence of the first three density coefficients could be made identical and could be qualitatively accounted for by making the diameter temperature dependent in the hard sphere theory of viscosity.

SECOND VIRIAL COEFFICIENT FOR MIXTURE

For evaluating the properties of low density binary mixtures, at least six constants have to be known if a two-parameter potential is used. Frequently the number of parameters is reduced to four by expressing the interaction of the unlike molecules in terms of the interaction of the like pairs. For mixtures of isotopes, and for such mixtures as *ortho* and *para* hydrogen, only the same number of parameters as in pure systems should be needed. By very accurate

measurements a 1 per cent difference was found (24) between *para* and normal hydrogen, the normal hydrogen containing the equilibrium concentration of *ortho*- or rotating-hydrogen. A similar effect was previously found in the viscosity. This large difference has not been accounted for theoretically. It should be explainable merely on the basis that the two forms obey different statistics and have different internal degrees of freedom. Frequently, however, by averaging over the internal degrees of freedom, the molecules are presented as having slightly different effective potentials. In this particular case, the effect of the non-spherical part of the potential on the interaction of molecules in different rotational states probably cannot be simply averaged out. On the other hand, the second virial coefficient of a binary mixture of hydrogen isotopes agrees with theory (25) within the experimental accuracy.

The interaction between two unlike molecules can, in a sense, always be considered as an acid-base interaction, because insofar as the molecules are different they have different electron attracting powers. This is also true of a pure system when the two different dipolar ends of two polar molecules interact. In these cases the wave function of the donor stretches in the direction of the acceptor and if the overlap of the wave function is large enough it is spoken of as a dimer or complex. Smaller distortions of the wave function are called collision complexes. The division between these classifications depends primarily on the time resolution and sensitivity of the observing instrument.

These "complexing" interactions are responsible for large deviations from the empirical rules for the potential between unlike pairs. These rules are that the length parameter of the two species should be averaged algebraically and the energy parameter averaged geometrically in order to get the parameters for the unlike interaction. The simple London dispersion theory shows that this is true only if the ionization potential and diameter of the two species are nearly the same (26). Applying the more elaborate rules to a hydrocarbon-fluorocarbon mixture improves the agreement for the second virial coefficient (26) but still leaves much to be desired. The potential will have to be further modified to account for the dominant surface interaction of the hydrogen and fluorines both by a Kihara-like correction and by a "complexing" correction. The relatively electron-bare protons could quite strongly distort the outer shell of fluorine electrons when the molecules are close together.

TRANSPORT PROPERTIES FOR DILUTE MIXTURES

Vapor diffusion experiments on hydrogen and nitrogen with cyclic molecules (27) show, for example, that the more elaborate combining rules do not always give better results than the geometric mean rule, and that for hydrogen the observed interaction is stronger (by almost 50 per cent) than the calculated one. An analysis of diffusion and thermal diffusion experiments for mixtures of helium, hydrogen, argon, and carbon dioxide (28) shows that the combining rules are as good as the intermolecular potentials themselves, which, however, are not fully satisfactory. By eliminating the potential

between the expression for diffusion and thermal diffusion, a useful relation between the two quantities is found. In view of the lack of information on the potential, this procedure might be pursued gainfully in other instances. Another study of diffusion in simple gas mixtures at high temperatures (29) shows that different interaction laws have about equal quantitative success, illustrating again the insensitivity of the results to the potential. An interesting experimental study on the measurement of gaseous diffusion coefficients of mixtures shows that the Kirkendall effect can be utilized (30). A report of the thermal diffusion in ternary mixtures demonstrates the effect of a third gas on the separation of isotopes (31, 32). The results qualitatively agree with the kinetic theory prediction that the thermal diffusion increases as the molecules of the added gas are lighter, smaller, and "harder" (steeper repulsive potential); the last factor being most important.

An interesting observation on the viscosity of mixtures of hydrogen and water is that the mixture has a higher viscosity than either pure component (33). However, this is predictable from the simple empirical combining laws. The viscosity of a carbon dioxide-nitrogen mixture shows a very large deviation from the usual combining rules (34), possibly because carbon dioxide has a large quadrupole moment, because the potential is not spherically symmetric, or because the complexing effect is appreciable or combinations of these limitations prevail. A good indication that the potential function is not known is that different properties require quite different parameters to fit the data. Even for the prediction of the viscosity of rare gas mixtures, the simple geometric mean law is off by 35 per cent for the xenon-helium system (35). Furthermore, the thermal conductivity was measured for the same rare gas mixtures and the dimensionless ratio of this to the viscosity multiplied by the heat capacity at constant volume was determined. The lack of agreement of this ratio with theory was again ascribed to the inadequacy of the combining rules. This ratio should be approximately 2.5 for pure monatomic substances, according to the kinetic theory. Based on the latest measurements, however, this is only approximately true (36). Another report (37) analyzes extensive recent data on the thermal conductivity of rare gas mixtures and develops useful empirical formulae for their calculation. Studies on the thermal conductivity of a binary mixture of a diatomic and monatomic gas shows that the internal structure of a molecule cannot be ignored since these internal degrees of freedom can transport energy (38). This is, of course, also true of a pure diatomic gas. Finally, the measured propagation of sound in monatomic gas mixtures has been correlated with the thermodynamic expression for the velocity of sound, in which both the molefraction average heat capacity and molecular weight have been substituted (39). Furthermore, the kinetic expression is satisfactory when the usual combining rules are used. In another ultrasonic study of a mixture of substituted methanes and rare gases the temperature dependence of vibrational collision lifetimes could be better explained by using a Kihara type of potential (40).

SPECTROSCOPIC METHOD

Much information has been gained about intramolecular potentials from spectroscopic methods. This same method could also be applied to intermolecular potentials. Indeed, some of the stronger complexes have already been investigated. These relatively weak interactions are sometimes instrumentally harder to detect, because the frequencies are in a less convenient range and the lines are not extremely sharp. Because of this, one often has to be satisfied with observing only a shift of frequency and a change of intensity and shape of the band. The most useful of these experiments for elucidating the potential of interaction between two molecules are those not involving an excited electronic state of the molecules, because from these experiments one learns only about the difference in the potential of interaction between the excited and ground states. The vibration and rotation bands are therefore the most useful.

How the bands for hydrogen chloride and acetylene change with a series of added gases has been studied experimentally (41 to 44). The data are complicated and largely unexplained; however, the shifts in frequency can be roughly correlated with the polarizability of the added gas and the broadening of the band depends on the rotational quantum number. No marked differences were found between acetylene and hydrogen chloride. This fact implies that in both cases the added gas interacts primarily with the proton, which, in the case of acetylene, must be rather acidic. A so-called self-shift of hydrogen chloride can also be observed. In the case of nitrogen and hydrogen (45), Vodar reports the existence of pressure-induced vibration and rotation lines. In order to explain these, the orientational fields as well as the anisotropy of the polarizability have to be taken into account.

In the same article, Vodar reports ultraviolet absorption data on benzene with added argon and nitrogen. Although both added gases have nearly the same polarizability, the shifts of the bands toward the red are very different. The order of magnitude of these shifts and the fact that helium causes a shift toward the blue, can be calculated from the London dispersion theory. The difference in the London force parameter between the excited and ground state is involved in the calculation. This same difference is involved in the quite elaborate calculation of the absorption of metal atoms with weakly bound, inert gas atoms. In the case of mercury (46) the line is considered as having a red wing caused by the statistical contribution of the interaction of free particles and also a fine structure on the blue side caused by the vibration and rotation of the weakly bound pairs. The parameters in the potential of interaction between the two atoms are evaluated from the shape and position of the band and their density dependence. It could be concluded that 0.673 per cent of the argon atoms were in a bound state at 325° K. and 1 atm. with mercury atoms. A similar analysis was carried out for the frequency shift and the hyperfine splitting of the alkali metals with rare gases as a function of pressure and temperature (47). In this case, instead of arbitrarily dividing the system into free and bound states, a Boltzmann distribution of

particles was used. Either method is satisfactory and which one is most convenient depends on whether the resolution is fine enough to see direct evidence of the dimer. The number of dimers calculated for such weakly bound systems will depend, however, on the method and time (frequency) of observation. In the case of the alkali metals also, when the lighter rare gases are added, the band shifts to the blue and the opposite shift is observed for the heavier gases. This is predicted from the interaction potentials. Although the parameters obtained for the potentials are not yet completely reasonable, a good beginning has been made toward obtaining information about the potential from spectroscopic measurements.

NON-PAIRWISE ADDITIVITY OF POTENTIAL

When more than two particles interact, the non-additivity of the potential can have significant effects, although its quantitative effect on properties is hard to estimate at present. Part of the difficulty is that it is impossible to separate the non-additivity of the potential from the uncertainties in the pair potential itself. Rigorous theoretical knowledge of non-additive effects is limited to the three-body calculation at large distances. Kihara (48) has shown that inclusion of this term for the third virial coefficient for rare gases improves agreement with experiment, and that the correction is not small. However, it is frequently argued that at higher density the effect is smaller, because an atom is then in a more symmetrical situation.

DATA ON RARE GASES

Nevertheless, the effect is not negligible for rare gases in the solid phase. These gases solidify in a face-centered lattice, but the computation of lattice sums for any pair potential that can be represented by any reasonable combination of inverse powers proves the hexagonal lattice to be slightly more stable. Hence the non-additivity of the potential must explain the discrepancy, although it is difficult to make a quantitative estimate. Further evidence comes from several sources for the well-studied argon system to the effect that in the condensed state the commonly used pair potential is inadequate, or the non-additivity effect is important, or both. By expressing the combined fluctuations of the internal energy and the virial in terms of thermodynamic properties and the exponents involved in the inverse power law of the potential, a lower bound can be placed on the repulsive exponent if the attractive exponent is six, since the fluctuations have to be positive (49). For liquid argon this exponent must lie between 13 and 14, and for the high temperature gas phase the value must be greater than 21. This is to be contrasted with the power of 12 that is often used; these findings are in agreement with the qualitative arguments, developed in the previous section, that the potential should be more like a square well. This expression can be generalized to mixtures. It would be desirable to know what effect a different attractive potential would have on the repulsive exponent, and, since the result is very sensitive to the accuracy of the thermodynamic data, how an error in the

data would affect the results. On applying the same theory to nitrogen and methane, similar results are obtained (50). In the gas phase at normal temperature the possibility of an exponent of 12 is not excluded.

A statistical mechanical analysis of thermodynamic crystal data makes it possible to study more critically the potential near its minimum (51). The potential is expanded about the minimum, and an anharmonic term is included. For the long range behavior the theoretical dispersion coefficient is used. As pointed out earlier, this coefficient is not reliable, although the present conclusions are not overly sensitive to this choice. These conclusions, again, are that the bowl is deeper and wider. Similar deduction can be obtained from shock Hugoniot data on liquid argon. These high pressure experiments test especially the repulsive part of the potential (52). The data show that the pair potential must be softer at low pressures and harder at high pressures. At high pressures the data seriously disagree with the potential deduced from molecular beam data. Since the Monte Carlo technique, which is rigorous once the pair potential is given, was utilized in the theoretical calculations, the disagreement must be traced either to inaccurate molecular beam data or to lack of pair-wise additivity of the potential, provided the shock data are accurate. That the assumption of pair-wise additivity becomes very serious at high enough pressures is evident from the fact that argon becomes metallic. In this paper (52) a commendable procedure is followed: for each pressure and property the weighting of distances in the potential is indicated.

CORRESPONDING STATES

There is further evidence in the corresponding state treatment of the rare gases that even for these simple systems the total potential of interaction is not well known (53). As implied earlier, the usual two-parameter potential does not fit accurately the second virial data for argon or xenon. Therefore it is not surprising that by using these two parameters to reduce the temperature and volume scale, the two equations of states do not coincide. This is especially true above the critical density and at low temperatures. If the critical temperature and volume are used as reducing quantities, agreement is improved as expected because these experimental quantities reflect the potential. If the critical volume is altered within the rather large experimental uncertainties, agreement can be still further improved (private communication from K. S. Pitzer). One further reason for the difference between argon and xenon is that quantum mechanical effects are not negligible, especially at low temperatures and high pressures (54). For example, to compress solid neon by 20 per cent requires 5000 atm. while for argon 15,000 atm. are needed at absolute zero.

The corresponding state treatment has been applied to the speed of sound in simple liquids (55). Since the speed of sound is simply related to the density derivative of the pressure (or the compressibility) this quantity is a more sensitive test of the validity of the corresponding state treatment. For ex-

ample, carbon tetrachloride deviates from the behavior of simpler liquids. The point is also made that the speed of sound at absolute zero gives a simple measure of the product of the exponents in the potential.

It seems that liquids should be segregated into classes, each of which obeys a corresponding state treatment by itself (56). Groups of molecules can then be recognized whose potentials differ, to a good approximation, by the values of only two parameters.

NON-SPHERICAL POTENTIAL AND INTERNAL DEGREES OF FREEDOM

There are many reasons for non-pair-wise additive potentials. For example, whenever the potential is not spherically symmetric, a third molecule will experience a potential with one of the other molecules which is different from the potential between an isolated pair. Thus if, for example, the same ends of two dipolar molecules attract each other, the average potential of the pair appears as a quadrupole to a third molecule at a great distance. Also, whenever there is a specific interaction between two molecules, a third molecule can not have the same interaction with both molecules of the interacting pair. Examples of this are recited in the next section on complexes.

The interaction of molecules in the condensed phase can also change the internal configuration of a molecule, and thus pair-wise additivity is destroyed. This effect in pure systems is demonstrated by substituted ethanes (57), and in a mixture by the long chain hydrocarbons in water and organic solvents (58). In the last system the distribution ratio between the two solvents mentioned can be explained on the basis of the difference between internal, torsional oscillation and hindered rotation of the hydrocarbon groups in water and in organic solvents, respectively.

POLARIZABILITY

The change of polarizability of a molecule by its environment also attests to the presence of non-additive potentials. The surrounding molecule distorts the wave function of another molecule, and hence a third molecule interacts differently with the original pair. Qualitative considerations indicate that the polarizability at low density should increase because attractive forces predominate and hence the wave functions spread out farther (59). When repulsive forces predominate, the opposite effect occurs. The latter effect is simulated but exaggerated when the calculation of an atom in a cage is carried out (60). For a pressure of about 5000 atm. this calculation shows that the polarizability has decreased by about 25 per cent. Attractive internal pressures of that magnitude exist in liquids, although changes of that magnitude are not likely in the normal state of simple liquids.

Polarizabilities are deduced experimentally from dielectric constant or index of refraction measurements. Unfortunately, the deviation from the Clausius-Mosotti equation are not only caused by changes in the polarizability but are also attributable to statistical fluctuation in the Lorentz local field. Nevertheless, the Clausius-Mosotti function for argon first increases in

the gas phase and then decreases at higher densities, and continues to decrease into the liquid region (61). These changes amount to only a few per cent however, with a 4 per cent jump in the index of refraction on going into the solid phase. The increase in the gas phase of a few tenths of 1 per cent for argon gas is confirmed by very precise measurements (62); whereas a decrease is found for helium, possibly because the attractive forces are smaller. It is pointed out that an analogy may exist in this behavior with the opposite shifts in the mercury line when these two gases are added, as noted earlier. Measurements on nitrogen and methane were precise enough to detect the presence of the quadrupole and octupole moments, respectively, and to determine for the first time a value for an octupole moment. Similar measurements on polar gases (63) show that the polarizability decreases with pressure although the interpretation is less clear-cut.

Dielectric measurements on mixtures which involve complexes like aluminum bromide in carbon disulphide or benzene show maxima and minima (64) as the concentration varies, as one might expect. For fluorocarbon-hydrocarbon solutions the polarizability of the mixture deviates from being mole-fraction additive in the polarizability of the pure components (65). The deviation amounts to about 1 per cent and changes sign as a function of concentration. On the basis of a fairly crude model, the argument is made that the polarizability of the fluorocarbon in solution increases by about 10 per cent, and that of the hydrocarbon decreases by a similar amount. This is qualitatively in agreement with the previous idea that the fluorine electrons are extended over to the hydrogens. Slight departures from linearity in mole-fraction were also found for the benzene-carbon tetrachloride system (66). More surprising was the independence of the polarizability upon composition, i.e., upon environment for the benzene-methanol system (67). This may be attributable to the way the data were analyzed, since the Böttcher equation, which includes an approximate reaction field, was used.

The optical activity of a molecule is very sensitive to changes in polarizability. In different solutions the optical activity can even change sign (68), and this phenomenon might be utilized to evaluate interactions in solution. In any case, it is possible that an effective pair-potential in solution can differ from the real pair-potential at low density by as much as 10 per cent and, as reasoned earlier, the effective pair-potential is likely to have the steeper sides of the bowl, that is look more like a square-well. At very high density, however, the effective pair-potential becomes less repulsive again, as judged by the Thomas-Fermi model, which predicts a repulsive inverse 7th power law.

SPECTROSCOPY IN SOLUTION

The purpose of spectroscopic investigations, so far as this review is concerned, is to learn more about the potential of interaction of a solute molecule with its solvent neighbors. Although no detailed information has as yet appeared, it has been possible to make progress by correlating and classifying the observed spectroscopic changes which occur upon solution. In the process

it has become apparent that the solvent can not be satisfactorily treated as a continuous dielectric, and that, in addition, specific interactions have to be taken into account in all but the most simple non-polar systems. In many cases the type of specific interaction involved could be learned.

Spectroscopic effects that can be expected upon altering the environment of a molecule include (69): (a) a modification of selection rules by a change of symmetry, (b) frequency shifts and intensity changes, and (c) the appearance of new absorptions such as combination bands (70). These and many other phenomena can be observed in a great variety of experimental situations. Environmental effects of solvent structure and specific interaction have been observed, for example, in optical rotation (71), in the Fermi resonance of polyatomic molecules (72), in Raman spectra (73, 74), and in microwave absorption (75). The microwave loss in liquid carbon disulfide has been attributed to collision complexes possessing dipole moments in which two molecules lie perpendicular to each other. Since microwave absorption is also observed in a benzene-carbon-tetrachloride solution, the existence of a dipolar complex can be inferred from this action as well as from the intensity changes of resonating intramolecular vibrations of carbon tetrachloride (76).

INFRARED

The effect of the medium on the vibrational frequency of a specific bond in the solute molecule can be learned from infrared studies without perturbing the absorbing molecule very much. Furthermore, the rotational freedom of the solute can be investigated. Cold or thermal neutron scattering can also give much information about motion in the liquid state. This rather difficult but interesting technique has so far been applied only to pure liquid systems. For example, in hydrocarbons it was found that the motion of the methyl group is relatively free (77), while in water the rotational motion is hindered (78). From infrared studies of acid halides and water in a variety of solvents the equivalent conclusion is drawn that, as the solute-solvent interaction increases, the rotational freedom becomes more restricted and eventually goes to libration (79). This restriction and eventual cessation of rotation is observed by means of the *Q* branch and the temperature dependence of the absorption (80) and, in the gas phase, by the pressure dependence of the more smoothed-out rotational bands (81, 82). As might be expected, nitrogen with its aspherical potential is more effective than argon in blocking the rotation of hydrogen chloride. In solid matrices of nitrogen the rotation of water monomers is also hindered, while in argon lattices the hindrance is much less (83).

The many studies of vibrational frequency shifts of polyatomic molecules in solution indicate that the solute-solvent interactions must include specific and local association effects and the "dipole moment" of the bonds on the surface of the molecule is the determining factor in the strength of the interaction. Thus, even though the dipole moment of a molecule such as acetylene is zero, a solvent molecule close to an acetylene molecule experiences the

local interaction of a hydrogen bonded to a carbon (84). The observed shifts increased as the donor strength of the solvent increases, and if there are two solvents present it is possible to detect two different shifts. The bond dipole moment is not even as significant as is the nature of the surface atoms themselves. This is shown by the good correlation achieved in the frequency shift of several X—H bonds when they are dissolved in the same solvents (85). Thus, the frequency shifts of one solute (where X is say, nitrogen) in a series of solvents give a linear correlation with the shifts in the same series of solvents when H is incorporated in a molecule bonded to carbon. This correlation does not work for C=O bonds versus C—H bonds, since the surface atom is different or the "bond dipole" is reversed, but it does work for C=O bonds versus S=O bonds, for example.

These shifts can be qualitatively understood in terms of bulk properties and specific interactions which involve more than just the long range point dipolar attraction (86). The bulk properties involve both the dielectric constant for the relatively slow motions of the solvent and the index of refraction for the faster electronic effects (87). Treating the solvent interaction more satisfactorily as a perturbation (to second order) on the internuclear potential of the solute, and considering dispersion, orientation, and repulsion energies, the calculated frequency-shifts were found to agree to within 30 to 50 per cent of those observed as opposed to the continuum dielectric theory which yields only 3 to 5 per cent of the experimental shifts (88). The shifts can also be correlated with the difference between the sum of latent heats of the pure components and the partial molal heat of mixing, provided that the solute latent heat is multiplied by a term indicative of its surface area (89).

Theoretically, the situation is quite complicated, as indicated by the correlation of the frequency shifts of the isotopes, hydrogen cyanide, and deuterium cyanide in the same series of solvents (90). The slope is 1.55 instead of 1. This article also gives an example of the site of preferred interaction of a solute on a polyatomic molecule that has several possible interaction centers. Thus, hydrogen cyanide prefers the halogen of a halogenated benzene molecule, while in pure benzene the molecule lies perpendicular to the benzene plane (91). This is inferred from the bending mode of HCN and the similar behavior of aromatic and aliphatic halides. Preferred interaction of iodine with carbonyl groups rather than other oxygens and π -electrons has been demonstrated (92). Evidence (93) has been found for the existence of a lithium bond analogous to a hydrogen bond. A study of the molecular addition compound of iodine and dimethylacetamide (94) shows distortion not only of the wave function of the bond to which the iodine is preferably attached (C=O), but also of bonds in the interior of the molecule (C—N).

X-RAY STRUCTURE OF COMPLEXES

The x-ray structure of complexes strikingly confirms that one is not dealing with chemically saturated species even when two non-polar molecules, such as 1,4-dithiane, and iodine interact (95). In that case the iodine mole-

cule is seriously distorted, as indicated by the fact that the interatomic distance is 0.11 Å greater than that in solid iodine. The boron-fluorine distance in BF_3 increases by a similar amount upon complexing (96). From other x-ray work (97, 98, 99) the impression is gained that the acceptor forms a "conductance bridge" between donors so that all the electrons are spread out as far as possible. Thus, a chlorine molecule lies perpendicular to the benzene plane connecting successive benzene rings; this explains why some of these systems have been found to be semiconductors and of fairly high conductivity (100).

The configuration obtained from x-ray studies makes it comprehensible why iodine can form a double complex with naphthalene (101) and why a benzene-hexafluorobenzene complex could be found (102). The spreading out of the wave function of the donor over the acceptor also manifests itself in the measured dipole moments of complexes. Metal halides in dioxane or nitrobenzene have dipole moments of several Debyes (103, 104). It is therefore reasonable to use an ionic model to explain the infrared frequency shifts upon complexing (105). It was possible to correlate the transfer of effective charge with the change of the force constant of the bond.

ULTRAVIOLET SPECTROSCOPY

As pointed out before, ultraviolet absorption involves electronically excited states and hence wave functions that are spread out and not characteristic of the normal ground state of the interacting particles (106). On the other hand, the wave functions are not so spread out that the solvent can usually be treated as a continuum having a dielectric constant (107). There is also the complication that the spectra can differ both in absorption and in emission, since in one case the ground state is in equilibrium with the solvent while in the other it is the excited state (108).

Nevertheless, it is possible to correlate frequency shifts both in the infrared (109) and in the visible (110) with the ultraviolet absorption. In the last investigation, two classes of solvents could be distinguished: those consisting of n -donors or of π -donors. Since the aliphatic hydrocarbons fell into the same class as the aromatic hydrocarbons, it might be best to put them in a third class because of the lack of filled electron shells on the surface atoms.

From studies of the much simpler system, mercury dissolved in liquid argon, a case is made for discrete sites in liquids (111). The spectrum of mercury in crystalline argon consists of a narrow triplet because the distorted cubic environment removes the degeneracy of the 3P state of gaseous mercury. In the liquid state this triplet is broadened into a single line, but an additional absorption appears at a lower frequency. This frequency is thought to arise because mercury is surrounded by two different cluster configurations. Before such things as the existence of mercury dimers and additional absorption of the simple mercury-argon molecule have been ruled out, this conclusion must be regarded as highly suspect. The mean position of the

absorption, and the width of the lines as a function of temperature, can be approximately interpreted in terms of the interaction potential provided account is taken of the modified motion of the solvent atoms (argon) surrounding the solute (mercury) atom (112). Even in the simple systems of pure rare gases the shifts are not yet explained. Thus, solid xenon has a lower absorption energy than gaseous xenon, while for krypton the shift is in the opposite direction (113). The extinction coefficient for oxygen in mixtures of argon and krypton depends non-linearly on concentration and is different for each gas (114).

To explain solvent effects for solutions of more complicated molecules it is again necessary to consider specific interactions and the nature of the surface atoms. The common analysis in terms of the ionization potential of the donor and the electron affinity of the acceptor is a crude measure of these effects. Thus, dioxane interacts specifically, although its dipole moment is zero (115), and the effect of branching or cyclization of a paraffin hydrocarbon solvent on the ultraviolet spectra of aromatic hydrocarbon can be detected (116). An example of the interactions studied by ultraviolet spectroscopy is that of gaseous oxygen in solution which can act as an acceptor and form weak complexes called contact charge transfer complexes (117). Again, carbon tetrachloride-benzene mixtures show evidence of deviation from the behavior of non-complexing systems (118). Iodine atom acts similarly to iodine molecule in its charge transfer behavior with benzene (119). This is not surprising, since the x-ray data for iodine mixed with benzene show that only one of the iodine atoms is in proximity to the benzene ring. Charge transfer absorption can also be detected within the molecule of formamide (120).

NUCLEAR MAGNETIC RESONANCE

Nuclear magnetic resonance spectra are strongly dependent on the solvent (121). This again shows that the electron distribution is perturbed upon solution, however, since the absorption frequency depends on the distribution of electrons relatively far away from the nuclei under study and upon many other factors, the interpretation of the shifts is complicated, and the shift is not a reliable indicator of the strength of interaction (122). Factors which must be considered are bond stretching, changes of polarity, formation of donor-acceptor bonds, the action of the electric fields, and the effect of unshared electrons (123). To that should be added magnetic anisotropy effects (124) and steric effects (125). This last paper concludes, from the different shifts of *meta* and *ortho* hydrogens in disubstituted benzene molecules, that there is preferred orientation of the solvent. From a study of solutions of substituted acetylene with benzene and mono-substituted benzene it can again be inferred by nuclear magnetic resonance that in one case the acetylene lies perpendicular to the benzene plane and in the other it interacts preferably with the substituted group (126). The above mentioned factors are also discussed with respect to a number of other systems (127 to 130).

EQUILIBRIUM THEORY

The statistical mechanical problem of determining the thermodynamic properties of condensed systems, given the pair-wise additive potential, has as yet been accomplished only semi-quantitatively. The problem is, of course, entirely mathematical but is so difficult that it has not been solved exactly, even for the simplest systems. The crucial problem is to find a good approximation to the exact solution. Several such attempts will be discussed.

One thing that has been accomplished in recent years is to get numerical results with which to compare the results of various approximations. Experiments on computers have made it possible to get accurate thermodynamic properties of systems at all densities whose potential is exactly known and is made to be exactly pair-wise additive. The two computational methods that have been utilized for this are the so called Monte Carlo (131) and the molecular dynamics (132) methods, both of which use simple spherically symmetric potentials. Both have also been extended to mixtures (131, 133) of hard sphere particles. Similar, though not quantitative, results can be achieved with physical models, such as the random shaking of glass beads (134). The volume of mixtures of beads of two different sizes gives some indication of the packing of hard spheres (135). The problem with such physical models is that it is difficult to know the effective interaction between the particles.

FREE VOLUME THEORY AND CLATHRATES

The simplest and historically earliest theories are what might be called one-particle theories. In these, one particle is treated in detail and the remaining particles supply a potential, which the one particle experiences. The free volume or cell theory is an example of this. Previously the remaining particles were put in some known configuration, usually a lattice, to evaluate their potential contribution. However, even with the best possible one-particle distribution function (136), such a theory is quantitatively inadequate. The free volume theory extends the crystalline phase into the low density region. Allowance for holes does not alter the situation, since the introduction of holes costs so much energy that too few to be significant are permitted to be present. Allowing the entire volume of the system to be accessible to the particle with another effective potential or mass rather than confining it to a single cell does not materially improve the theory (137). The theory is strictly valid only for high density solids where correlation between the motions of neighbors becomes unimportant. A quantum mechanical version of the simple free volume theory has been numerically applied to solid hydrogen and deuterium (138).

When this theory is extended by treating two particles in detail, formidable mathematical problems appear. The cell cluster theory is formally exact in that it treats successively larger clusters of particles in the average potential of the rest (139) and thus systematically takes into account correlation between the motion of a larger number of particles. The extension to

mixtures (139) is particularly necessary because there the higher cell cluster correction will be large, since the usual initial choices of equivalent lattice sites and random contacts for the two different molecules are poor approximations. It is necessary as a first approximation to assume equal cell sizes for different molecules, because the most efficient packing of two different sized particles is an unsolved problem. However, even the cell cluster theory of two particles is complicated enough, and can be solved only approximately. Although these first corrections to the simple cell theory are in the right direction, they are too small and hence it appears necessary to evaluate clusters containing a particle and all its nearest neighbors. A variational treatment of finding the optimum two-particle cell function is also formally exact when extended to more particles, but it also runs into mathematical complications (140). Lattice gas theories have been extended to let the number of particles in each cell be artificially not just an integer but any real number (141). The results are still artificial. In order to get realistic results for lattice gases it might be worthwhile and feasible to investigate further the question of how many lattice sites are necessary for a given number of particles. The continuum theory is approached if the lattice is fine enough. An interesting extension of the cell theory is made by considering the system to be composed of sub-units which can be treated exactly (142). Using lines of hard spheres, good results are obtained.

The experimental situation for which the simple cell theory is most applicable is presented by clathrate compounds (143), where singly and weakly bound solute molecules are held in a rigid structure. The lattice free energy is assumed to be independent of solute occupation, although the infrared absorption spectrum of urea-hydrocarbon adducts shows that in some cases there is distortion of the lattice (144). The same conclusion has been reached from a study of the heat capacity and entropy of methane in the quinol clathrates (145) in the temperature region of 13 to 298° K., namely, that methane interferes with low frequency lattice deformation vibrations and that these deformations are different from those of the argon clathrate. After taking into account the internal vibration of methane at high temperatures and the restricted rotation of the molecule at low temperatures, the thermodynamic functions can be calculated within about 10 per cent. Part of the disagreement stems, no doubt, from the estimate of the potential of interaction in the cavity surrounded by several different kinds of atoms and the estimate of the equivalent spherical size of it from x-ray data. The geometric mean rule is used to find empirically the energy parameter of the cavity potential for one gas; this same parameter is then used for other gases. The theory nevertheless has predictive value. The hydrates of oxygen and nitrogen experimentally (at 0° C.) have equilibrium pressures of 120 and 160 atm. respectively; the theory predicted 63 and 90 atm. (146). Improvement in the theory may come from considering the restricted rotation of the diatomic molecules near the walls of the cavity. A more complicated clathrate of sulfur hexafluoride with dianin has been found in which two molecules

are in a cavity, but again infrared data show that the interaction with the cage is slight (147). Rare gas clathrates, composed of mixtures of water with organic compounds (148) have been studied, as well as hydrocarbon inclusion complexes with methylnaphthalenes (149)

SCALED PARTICLE THEORY AND GAS SOLUBILITY

This theory yields a consistency relation that must be obeyed by the exact radial distribution function of a system with pair-wise additive potentials. This relation is obtained by equating the statistical mechanical expression for the pressure with the one derived from the volume derivative of the chemical potential. The chemical potential is evaluated by means of the work or free energy required to create a cavity for an additional particle as a function of size (150). Other consistency relations with the pressure, involving the compressibility derived from fluctuation theory, have previously been used.

It is possible to evaluate the work of cavity formation for hard spheres when the cavity is small and to use macroscopic arguments when it is large. The consistency relation then allows interpolation for intermediate sizes. The work to make small cavity sizes can be evaluated up to the point where more than one particle center can be inside the cavity. After that, integrals must be evaluated very much like the ones for the cell cluster theory. Some progress into this region can be made by using continuity of derivatives at that particular cavity radius. For particles which have soft repulsive potentials, the theory becomes very much more complicated because, strictly speaking, more than one particle center can be inside even a small cavity. The theory is also particularly well suited to the hard sphere systems, because only one parameter has to be determined as a function of density (the radial distribution function at contact, or the mean free path). For hard spheres, the theory gives the correct first few virial coefficients and does well in reproducing the fluid region of the system, but it fails to account for the solid region.

The theory has been extended to dilute mixtures for real systems by adding an attractive part as a perturbation to a hard sphere core (151). The work of cavity formation involves the surface tension; for small cavities this is an approximation to the changed motion of the solvent surrounding the solute. The theory seems to work moderately well when applied to gas solubility for the quoted system of helium in benzene and also does fairly well for helium in argon. In the case of argon in benzene, compensating errors must again occur, while for argon in carbon tetrachloride the solubility is off by a factor of 10^6 . These results are tentative, because the attractive potential is added as a perturbation.

The simple cell theory applied to the gas solubility of argon in carbon tetrachloride does not do much better, even if the number of nearest neighbors is adjusted so that the virial theorem in the cell of a size corresponding to the measured partial molal volume is obeyed. With about eight neighbors,

the solubility is off by a factor of approximately 10^3 . It is necessary to take into account the changed state of the molecules surrounding the solute by adding what is often called energy of cavity formation in gas solubility theory and earlier was called surface tension. Reasonable values for these energies then give a good theoretical estimate of the solubility.

By essentially measuring the cell size and then adjusting the number of nearest neighbors, one obtains molal free volumes of several cubic centimeters, whereas free volumes for pure liquids or liquid mixtures are usually less than 0.1 cc. The theory is thus much less sensitive to errors in the cell potential and in the configuration of the solvent. Furthermore, these dilute solutions do not require that an arbitrary distinction be made between wandering and lattice atoms (152). The quantum corrections to the free volume theory have been worked out in an attempt to explain the fact that deuterium is approximately 20% more soluble than hydrogen in liquid argon, (152). The agreement obtained is not very satisfactory, because the cell potential was treated as a harmonic oscillator in spite of the large free volume, the number of nearest neighbors were not adjusted, and the quantum effect gives a considerably different partial molal volume, and hence cell size, for the two isotopes (greater than 10 per cent). As a result, not only the free volume but the energy of void formation, for example, are different in the two systems. Several additional gas solubilities are considered (153 to 155).

SUPERPOSITION THEORY AND RADIAL DISTRIBUTION FUNCTIONS

The superposition theory represents another attempt to take into account pair correlations and to approximate higher correlations. The theory could be carried to higher approximation but only at the cost of great mathematical difficulties. A comparison of the radial distribution function from the superposition theory with the accurate one from the Monte Carlo method shows large discrepancies at high density (156). A comparison with the Mayer cluster expansion shows that only clusters of singly connected ring diagrams are taken into account in the linearized superposition theory (157) and that the singularities in the theory are due to the approximations and are unrelated to phase transitions (158). Using the superposition theory in the expression for the fluctuation in the coordination numbers of nearest and next nearest neighbors, it is found that they are opposite to each other and large, 20 and 50 per cent respectively of the average coordination number for rare gas liquids (159), and that pressure and supercooling do not affect these results very much. These results argue against the hypothesis of quasi-crystalline arrangement of particles in the liquid state. On the other hand, for short times such as 10^{-11} sec., and for molecules with a strong directional force similar to that of water, neutron diffraction does support the quasi-crystalline model (78). For such short times a molecule is surrounded by the same neighbors until it diffuses by small step motions. There is also much evidence from x-ray, electron, and neutron diffraction that the number of nearest neighbors in metallic and non-metallic liquids is less

than 12 (160 to 162). It must be pointed out, however, that the number of nearest neighbors can vary considerably, depending on how the area under the first peak of the radial distribution function is calculated (163, 164). The last mentioned article points out that, for sodium-potassium alloys, deviations from random mixing are small. This is also true for other alloys (165, 166). For still other alloys, however, microheterogeneity could be detected showing deviation from random mixing (167 to 170).

HYPERNETTED CHAINS AND CRITICAL PHENOMENA

The hypernetted chain approach is being actively worked on by several groups and involves successive summations of different sets of Mayer diagrams, namely those that can be convoluted (171 to 173). It is hoped that this series will converge faster than the usual density expansion, but numerical results have not yet appeared. The theory has been generalized to mixtures (174) and, when linearized, leads to the linear superposition theory (175, 176). The theory has been used to calculate the first correction to the superposition approximation (177).

The theory is claimed by some to be consistent (178) and by others to be inconsistent (179) with the Ornstein-Zernicke integral equation. The argument concerns the large-distance behavior of the radial distribution function $g(r)$ near the critical point, where long range correlations exist. The Ornstein-Zernicke behavior is

$$o(r) - 1 = \frac{e^{-kr}}{r}$$

This equation has been derived by various means (180) including macroscopic arguments for a non-uniform density medium. By leaving out the terms in the hypernetted chain theory which are difficult to calculate, Green arrives at

$$g(r) - 1 = \frac{1}{r^2}$$

At the critical point of a mixture it has been shown (181) that the three separate radial distribution functions of this mixture all have the same form at large distances and differ only by a scale factor. Empirically analyzing experimental data, the following, again different, behavior is found:

$$g(r) - 1 = (1 - b^2 r^2) e^{-a^2 r^2},$$

where a and b are constants.

Through the use of small angle x-ray scattering, evidence of non-uniform densities or clusters is found in systems near the critical point. These clusters increase in size as the temperature or concentration approaches the phase separation region, and they are no longer detectable by x-rays when one is about 20° to 30° above the critical point (182). The interpretation of the data in these dense polydisperse systems with a distribution in size of scattering centers is not simple. These "quasi-emulsions" have been studied

by x-rays in other systems (183 to 185). In the last paper (185) it is reported that the local "demixing" could be detected out to the fifth neighbor near the critical temperature and only to the first neighbor 30° above that.

Experimental studies near the critical point are difficult because of the length of time required to establish equilibrium. The cause of this can be explained in terms of the vanishing of the diffusion coefficient (186) because Fick's law is no longer obeyed, since the derivative of the chemical potential, with respect to the number of solute particles, vanishes (187). At the critical point the second derivative vanishes also, but how many more derivatives vanish is a moot question. Some say that the fourth derivative is discontinuous, with a reversal of sign, (188) but the assertion is based on data taken rather far removed from the critical point in a complicated system; based on no better data (189, 190), others say that the third derivative is not zero; and still others say the third derivative is zero over a limited concentration region (191, 192). An interesting suggestion, is that some kind of transition persists above the critical point (193) (the "derby hat" region of the Mayer theory) and that in that region the third derivative varies strongly. The experimental basis of this idea is the x-ray work mentioned before and, among others, the fact that the maximum in the heat capacity does not diminish until the temperature is 5° to 10° above the critical point.

Whether there can be limited mutual solubility of two gases above the critical temperature of the less volatile component is answered positively from experiments on nitrogen and ammonia in one paper (194) and negatively in another (195). Theoretically, the criteria are set up for such an eventuality in terms of the van der Waals equation (196). These considerations show that a polar and a non-polar gas, or even two non-polar gases such as helium and carbon dioxide, can coexist as separate phases as long as the attractive forces are sufficiently different and the diameters are nearly the same. The latter restriction is theoretical since the effect of various arrangements of the particles in the mixture was inadequately treated. In liquid systems three phases have been found to coexist above the critical temperature of two of the binaries (197). The limited solubility of nematic and smectic liquid crystal phases has been found, but nematic phases as well as smectic phases mix completely among themselves (198). In the nematic phase one rotational degree of freedom has been frozen out, while in the smectic phase one additional translational degree of freedom is frozen, thus forming a layer-like structure. The impossibility of infinite solubility of even- and odd-numbered solid hydrocarbon solutions has been experimentally established (199).

REGULAR SOLUTIONS

Since the cell theory, the corresponding state theory, and the conformational solution theory, as well as their applicabilities, have recently been well discussed in *Quarterly Reviews* (200), these subjects will not be considered here in detail. It is worthwhile, however, to point out how well most systems

correspond to the behavior of regular solutions; that is, the excess entropy of mixing is small when the volume is held constant. This is even true a few degrees above a phase separation point, and it is also true in other systems, in spite of the molecules' having different attractive fields and sizes, as long as complexing systems are excluded. The correction of the entropy, from constant pressure to constant volume, is essential to the definition of regular solutions and brings about significant improvement in compliance with regular behavior (201, 202). The cell theories frequently consider the cells of the two species to be of equal size for mathematical convenience as mentioned earlier, and, although this corresponds to mixing at constant volume, the initial pressures are artificially different (203).

Thus, the xenon-argon system, for example, has a fairly large partial molal enthalpy (630 cal./mole) yet the excess entropy is nearly zero (204). This is true in spite of limited solubility in the solid phase (205). The critical point for these rare gas mixtures is predicted fairly well by the cell theory after the value is reduced by about 25 per cent to make allowance for the assumption of random mixing. However, the experimental data seem to be in doubt. For the argon-krypton system the theory predicts 44°K. for the critical temperature and the experiment is claimed to give $56 \pm 8^\circ\text{K.}$ (205). From heat capacity measurements, the conclusion is drawn that the phase transition must occur below 12°K. since between 12°K. and 40°K. no evidence of separation could be found, and above 60°K. vapor pressure measurements and regular solution theory do not predict separation (206). There may be some difficulty in establishing equilibrium. For the liquid argon-krypton system, the calculated excess entropy is small, and the measured excess partial molal free energy agrees roughly with the cell theory (207). A practical method has been presented for computing excess free energies from the dew curve (208).

Many systems in addition to those consisting of the rare gases have been studied and show nearly regular solution behavior. Even if there is evidence of a weak complex, such as in the carbon tetrachloride-benzene system, the solution can be nearly regular (209). The entropy of fusion is a good indicator of whether a complex survives the melting process (210). In non-complexing systems, concentration fluctuations caused either by different sizes and shapes of the molecules or by different types of intermolecular potentials are the main cause of deviation from regular solution behavior (211).

CONFORMAL SOLUTIONS AND ISOTOPIC MIXTURES

As an example of applicability, the conformal solution theory might be used successfully in the treatment of isotopically substituted classical fluids (212). By integrating over the internal coordinates of the molecules, the isotopes are found to have only slightly different effective potentials. For mixtures of light isotopes, however, the zero-point energy causes the pure isotopic liquids to have very different properties, so the theoretical problem of explaining the excess thermodynamic functions upon mixing is in not

completely satisfactory shape. Prigogine's theory properly predicts positive deviations from Raoult's law for isotopic mixtures of both hydrogen and helium, and the phase separation for helium isotope mixtures (213). The quantitative aspects of the theory are somewhat unsatisfactory because it is necessary to extrapolate properties of the heavier isotope to rather large negative pressures in order to get the properties at the measured molar volume of the mixture (214). The excess volume and free energy for the isotopic helium mixture are predicted within about 50 per cent, while the excess entropy is worse. The experimental entropy changes sign with temperature. The mixture hence is nearly regular in that region, although the phase separation curve is not quite symmetrical about the half mole fraction point (215).

For hydrogen-deuterium liquid mixtures, the excess volume as predicted by the theory has the wrong sign, while the excess enthalpy is within 30 per cent (216). As for a phase separation point, the theory predicts a temperature of less than 1°K. Experimentally, the situation is confused by the different and apparently unknown crystal structures of hydrogen and deuterium (217 to 219), but the phase separation occurs at a much higher temperature.

Improved calculations on liquid *ortho*- and *para*-hydrogen have been made (220). With respect to the liquid-vapor and liquid-solid transitions of helium, although it applies to any substance, the point has been made that at constant volume these are second order transitions in the Ehrenfest sense (221). Finally, the following general principle has been established with respect to two species of isotopic elements: the isotope effect of the first element upon the separation factor of the isotope of the second element is the same as that of the second element upon the first (222). Thus, for example, the ratio of the vapor pressure of $N^{14}O^{16}$ to that of $N^{14}O^{18}$ is the same as that of $N^{15}O^{16}$ to that of $N^{15}O^{18}$ (223, 224).

TRANSPORT THEORY

The major calculational advance in transport theory in recent years has been the formulation of the transport coefficients in terms of autocorrelation functions. A very neat derivation of these expressions for multicomponent mixtures has recently been given (225). The expressions are equivalent to the usual expression in terms of averages over the non-equilibrium distribution function, but may be easier to approximate and to use, since they involve only equilibrium distribution functions and fluctuations about the equilibrium state. They do not solve the basic problem of irreversibility.

The auto-correlation function approach has been used to study the dielectric relaxation of polar liquids (226), the motion of a heavy particle in one dimension (227), the frequency dependence of the transport coefficients (228), the corresponding-states principle for transport properties, which is nothing more than a dimensional analysis (229), and the diffusion coefficient (230). "Auto-correlation" means that it is necessary to know a given prop-

erty of the system at different times. The radial distribution function at two different times has been investigated (231). When, for example, the decay of the auto-correlation function of the velocity, needed for the diffusion coefficient, is assumed to be exponential, the same expression results as from the Boltzmann equation. In dense systems of hard spheres the auto-correlation expression yields the same results as Enskog's modification of the Boltzmann equation. However, at higher densities the assumption of exponential decay is no longer valid, and triple and higher correlations have to be considered. It is claimed that these corrections have been evaluated by studying the Enskog modification of the Boltzmann equation for mixtures of spheres (232). In fact they have not, although these corrections would appear as corrections in a power series in density just as in the virial expansion. Longuet-Higgins and Pople (233) in their theory, on the other hand, have not even assumed an exponential decay of the auto-correlation function, but have dealt only with its initial value.

The transport properties of liquids in relation to their structure are discussed in a recent *Quarterly Reviews* issue (234). It is pointed out that transport coefficient ratios for isotopically substituted molecules can illuminate the transport mechanism (235). For spherical molecules like methane the ratio is given by the square root of the masses, while for aspherical molecules, such as water and benzene, it is given by the ratio of the principle moments of inertia, indicating that relaxation is by rotational rather than by translational motion. However, different transport properties for a given substance do not always have the same mechanism. For water, the thermal conductivity is given by the ratio of the square root of the masses.

DIFFUSION

From a theoretical study of the diffusion coefficient in binary liquid mixtures, the conclusion is drawn that if the solution is regular the two self-diffusion coefficients are in the inverse ratio of the molar volumes (236). Experiments in a rather complex system, however, show the ratio to be nearer to the cube root of molar volumes, which agrees with Einstein's prediction. In diffusion experiments the frame of reference has to be considered, especially if there are volume changes upon mixing (237).

The self-diffusion coefficient is theoretically the easiest to evaluate and the most fundamental, since all other transport coefficients have been related to it. It is therefore important that the experimental task of obtaining it has been lightened considerably through the use of a nuclear magnetic resonance technique (238). Using conventional techniques, the self-diffusion coefficient of argon has been remeasured and found to be 20 per cent lower than before (239). The lowest value is usually the correct one. The diffusion of liquid krypton and gaseous hydrogen in liquid argon led to the same activation energy for diffusion as for self-diffusion, but to different frequency factors (240). It seems that the critical energy for diffusion is determined solely by the solvent, which is the energy necessary for a density fluctuation that allows the solute to escape its temporary environment. The variation in the

pre-exponential factor, representing the frequency with which the solute attempts to move in the direction of the density fluctuation, could be explained by assuming the solute was coupled to only one solvent molecule. The results show again the amazing applicability of the Stokes-Einstein relation to particles of molecular dimension.

The isotope effect in the diffusion of lithium in both silicon (241) and tungsten (242) shows that since the diffusion coefficients are in the ratio of the square root of the masses, the interstitial mechanism of diffusion predominates. Similarly, the self-diffusion coefficient in liquid hydrogen and the diffusion coefficient of deuterium in hydrogen have roughly the same activation energy, while the pre-exponential factor is again in the ratio of the square root of the masses (243). The general problem of relating isotope diffusion to self-diffusion with quantum mechanical corrections for helium has been discussed in a similar way (244).

VISCOSITY AND THERMAL CONDUCTIVITY

The viscosity of isotopes has also been found to be proportional to the square root of the mass (245) although for the complex molecules used this should not always be the case (see earlier discussion). The results have been criticized (246). The viscosity of the normal component of the isotopic mixture of helium seems to obey Poiseuille's law, and the minimum in the viscosity at a concentration of 10 per cent of the lighter isotope is theoretically accounted for (247). Finally, a statistical mechanical theory of the viscosity was able to give an analogue to the Stokes-Einstein equation for binary liquid mixtures (248). The product of the self λ -diffusion coefficient and the viscosity is independent of the composition if the solution is regular, since then the radial distribution function is independent of composition. However, some other assumptions were necessary, the most serious being that the pair friction tensor is independent of particle separation.

The thermal conductivity of mixtures of isotopes in the solid phase behaves quite differently from that of the pure isotopic substances which have been found, as noted earlier, to be in the ratio of the square root of the masses. A small amount of the light helium isotope added to the heavy isotope in the solid decreases the thermal conductivity by a factor of 5 (249, 250). This is because the added isotope acts as a scatterer to the vibrational modes that carry the thermal energy. Whether this occurs also in the liquid depends on the mechanism of heat transport.

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ELECTRODE PROCESSES¹

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This review covers the period from the last review in this series on the same subject [Delahay (1)] to autumn 1960. In some cases earlier papers will be quoted, especially if they pertain to fields not reviewed in earlier articles.

A great deal of personal freedom has been exercised in selecting special papers for review and the author wishes to apologize for having omitted a number of interesting contributions to this subject, because of either space limitation or a lack of awareness of their existence. The field of electrode reactions in molten salts and nonaqueous solvents, although of growing interest, has been largely excluded because of the limited space.

The main areas of progress in research on electrode processes will be outlined briefly at first. Theoretical interest has been concentrated primarily on the relations between double layer structure and electrode reaction kinetics, including the effects of specific adsorption at the electrode surface. Fundamental contributions have been made to a better theoretical understanding of redox reactions which are different in mechanism from ion transfer reactions because the transfer of electrons through the interface occurs via a tunnel effect. Promising steps have been made in the application of ligand field theory and molecular orbital theory to problems concerning the discharge of complex ions, or electron transfer from and to organic molecules. This has resulted in very promising correlations between structure and kinetics.

The problem of crystal growth or crystal dissolution during electrolysis has received new impetus from considering the contribution of screw dislocations to this process. Unfortunately all the experimental investigations in this field suffer from a disparity between the conditions of experimental research and the highly idealized models of the theories, which makes it very difficult to reach definite conclusions.

A new field, introducing some novel theoretical concepts into this subject, has been developed in the application of high-purity semiconductor single crystals for electrode reactions. This may be able to help solve the old problem of passivity of metals, and can give new insight into the correlation between the structure of solids and the course of reactions on their surfaces. Also, the broad direct research on passivity and on the electrolytic formation of protecting surface layers on metals has brought to light many important results, completing our knowledge of the general features of such electrodes and of the very individual properties of special systems.

The development of experimental techniques for studying more precisely the kinetic parameters of electrode reactions has continued to reach higher resolution for very fast reactions. In this connection, transient phenomena

¹ The survey of literature pertaining to this review was concluded in October 1960.

under special experimental conditions have been analysed, often with great mathematical ingenuity, for numerous combinations of preceding, succeeding, or catalytic reactions with one or more charge transfer processes involved. The rotating disc arrangement has also proved a highly effective tool for the study of electrode reaction kinetics.

By means of these methods a great number of special electrode reactions have been investigated and our knowledge of mechanisms has increased rapidly.

GENERAL PROBLEMS

ELECTRICAL DOUBLE LAYER

Double layer structure.—The general concepts of Helmholtz, Gouy and Chapman, and Stern for the treatment of double layer theory and the extensions by Grahame, Frumkin, Esin and Markov [as reviewed by the late D. C. Grahame (2)] have demonstrated their great value. Reviews on the role of the electrochemical double layer in electrochemistry have been given by Frumkin (3). The theory allows interpretation of double layer capacity measurements at mercury electrodes [Grahame *et al.* (4, 4a)] although a number of details remain in doubt. Some important correction terms have been discussed in the theory of double layer structure. The rediscussion of the "discreteness of charge" effect for the inner double layer by Grahame (5) and Parsons (6) and the papers on the influence of ion size and dielectric saturation for the diffuse part of the double layer by Brodowsky & Strehlow (7) and Sparnaay (8) may be mentioned.

The special shape of differential capacity-potential curves in aqueous salt solutions (the bump in the curve) has been attributed by Grahame (4) to the influence of water structure in the double layer, because it cannot be found in nonaqueous solutions or salt melts [Minc & Jastrzebska (9), Randles & White (10)]. Recently, Watts-Tobin (11) has attributed this bump to relaxation of water dipoles in the Helmholtz double layer.

The question of double layer structure under nonequilibrium conditions, i.e., under d.c. or a.c. flow, which is very important for kinetics, has been treated by Levich (12) and Spaarney (13). They have shown that under d.c. flow important deviations from equilibrium distribution can occur with high field strength in the diffuse double layer, or for high currents. The earlier results of Ferry (14), which state that the relaxation times for the diffuse double layer under a.c. flow should be of the order of 10^{-7} sec. for 10^{-3} *N* solutions, have also been confirmed by these authors.

An important field for the application of double layer theory has been found in the semiconductor-electrolyte interface as shown by Bohnenkamp & Engell (15) for germanium, by Dewald (16) for zinc oxide, and as discussed theoretically by Green (17). In these systems, the double layer in the solid is very diffuse. Capacity measurements give information about the distribution of charge.

Adsorption of ions.—That the adsorption of ions cannot follow a simple

Langmuir-isotherm is obvious since strong mutual interaction between adsorbed ions and with other electrical charge carriers must occur. The adsorption, therefore, depends heavily on the net surface charge at the electrode. The thermodynamical expressions for ion adsorption at metal electrolyte interfaces have been thoroughly discussed by Parsons (18), who has reached good agreement for the interpretation of some experimental results by making use of a second virial coefficient in the two-dimensional equation of state for the surface pressure. This is equivalent to taking into account the direct interaction between next neighbours of the adsorbed species. Not only inorganic anions can be specifically adsorbed at the metal surface, as assumed for some time, but also inorganic cations. This has been shown by the school of Frumkin for some large cations [e.g., Frumkin *et al.* (19, 19a, 19b)]. Adsorption isotherms for large organic anions (polyacids) have been studied by Miller & Grahame (20), and for tetraalkylammonium-cations by Frumkin & Damaskin (21).

The interpretation of adsorption measurements at solid electrodes is more difficult than that using liquid electrodes. Although the general conditions are equivalent, great complications arise from surface roughness and specific surface structures that are not easily controlled. Even so, the investigation of solid electrode adsorption behaviour remains an important task [e.g., Popat & Hackerman (22), Chuang-Hsin & Iofa (23), Brintseva & Kabanov (24)].

Adsorption of surface active materials.—Parsons (25), using a rigorous thermodynamical basis, has discussed the problems involved in deriving the amount of adsorption from differential capacity measurements in the general case and especially for neutral molecules. Only for very limited types of adsorption isotherms (e.g., in the region of Henry's law) can a linear relation between differential capacity and amount of adsorbed molecules be expected. Adsorption isotherms for a number of organic molecules have been studied by Laitinen & Mosier (26) and Breiter & Delahay (27).

The kinetics of adsorption of surface active molecules and their dependence on double layer charge, which form the basis for the analytical application of tensametric waves as introduced by Breyer (28) and reviewed recently by Bauer (29), have found further interest during the review period. Lorenz (30) has extended his treatment of adsorption processes under alternating current to more complicated cases, e.g., association of adsorption molecules in the surface, and has measured the rate of adsorption and association in some suitable systems. The kinetics of adsorption at electrodes under pure diffusion control, important for the contamination of electrodes in very dilute solutions of adsorbents, have been discussed by Delahay & Fike (31).

Zero point of charge.—The knowledge of the potential of zero charge on the electrode for the various materials is very important for the understanding of correlations between double layer structure and the kinetics of electrode reactions [cf. review papers by Frumkin (3)]. A collection of results for various metals has been given by Antropov (32). Especially interesting is an

investigation by Kusnezov *et al.* (33) on the change in the zero charge potential when two materials with very different zero points are alloyed. An ingenious new method for determining zero points of charge has been applied by Voropajeva, Deryagin & Kabanov (34), who used the mutual repulsion, which shows a minimum at the zero point, of two equally charged diffuse double layers as an indicator.

THEORETICAL KINETICS

Charge transfer reactions.—The kinetic aspects of the charge transfer through the double layer by means of ions has not undergone any radical change, but the time approaches when we may have a better understanding of the properties of the activated complex in this reaction step. In a series of papers, Vlček (35) has discussed the correlations between electronic configurations of possible intermediates and the rate of discharge of complex ions of nickel, cobalt, chromium, manganese, europium, and rhenium, by applying the principles of ligand field theory to the electron orbitals of these complexes. In principle, the same can be done for every solvated ion that has strong solvation bonds.

The question that has been debated for many years, of whether tunneling contributes to an ion transfer process, has found attention again; the hydrogen transfer reaction is discussed by Christov (36) and by Conway (37).

There can be no doubt that tunnelling is the mechanism for electron transfer in redox reactions at electrodes. Marcus (38) has shown that the theoretical treatment of electron transfer between ions in solution, which is based on the application of the Franck-Condon principle, can also be applied to electron transfer at electrodes. The writer himself (39), starting from principles given by Gurney (40), has developed a statistical treatment of redox processes at electrodes that allows introduction of the electronic structure of the solid into the kinetic relations by means of the "band model theory." This treatment is especially valuable for the understanding of redox reactions at semiconductors, where it can be shown that one has to distinguish between electron transfer from and to the conductance band, or from and to the valence band [Dewald (41), Gerischer & Beck (42)].

Marcus (38) and Hush (45) have discussed the problem of whether electrode reactions occur adiabatically. They came to the conclusion that this can normally be assumed.

Electron transfer to organic molecules can also be correlated to molecular orbital theory. This has been discussed in a number of important papers for aromatic compounds and molecules with conjugated double bonds by Hoijsink and co-workers (43, 44). Hush (45) has applied molecular orbital theory to the polarographic reduction of methyl halides, and Fueno *et al.* (46) have presented analogous considerations for vinyl compounds. Relations between reduction potentials and excited electron states in the organic molecules play an important role in these theories. Such relations have been discussed and experimentally demonstrated by Brück & Scheibe (47) and Grabovski (48).

Electrolytic crystal growth and dissolution.—Our knowledge of the mechanisms of electrolytic crystal growth has remained far from satisfactory, even though important new ideas have been introduced. First must be mentioned Vermilyea's application (49) of the Frank-Burton-Cabrera model which describes the role of screw dislocations in crystal growth to the case of electrocrystallization. The importance of adsorbed atoms on the surface in the crystallization process has been experimentally demonstrated by Mehl & Bockris (50), Lorenz (51), and Gerischer (52). It appears obvious that nucleation and growth of higher index faces (which do not need two-dimensional nucleation, as often emphasized by Stranski for general crystal growth problems) play a very important role in most cases of electrolytic crystal growth.

Details of such observations will be treated later. One case of unusual crystal growth and nucleation has been investigated by Fleischmann & Thirsk (53) who studied the anodic crystallization of lead dioxide. They discuss the possible experiments, especially transients analysis, that can give information on crystal growth kinetics in general.

Influence of double layer structure and adsorption on kinetics.—The first theoretical approach to the influence of double layer structure on kinetics, given by Frumkin in 1933, has proved its value in many later studies though the original theory needed further improvements to explain a number of detailed complications. These improvements have been developed to a great extent by Frumkin and his school (3, 54). To the original idea, that the concentration of ionic reacting species at the interface should depend on the potential difference in the diffuse double layer (according to a Boltzmann equilibrium distribution of the charged particles), had to be added the possibility that all kinds of interaction between ions of opposite charge (e.g., ion pair formation) should occur, especially in the inner region of the double layer where the ionic concentrations become very high when the potential is displaced from the zero point of charge.

A further possibility is that the double layer is not at equilibrium, and the movement of negatively charged ions is hindered by the electrical field of the diffuse double layer. Levich (55) has introduced this assumption to explain the retardation of some anion reduction when the charge on the metal is negative. This approach has been rediscussed by Gierst (56), who has also shown how both approaches can be combined in a united theory. A similar discussion has been given by Levich (57), himself.

Frumkin has given both experimental and theoretical arguments to explain why the effect of Levich, which needs high potential differences in the diffuse double layer, should not be effective in most cases. Most of the observed effects seem explicable using the original assumption of Frumkin and the modifications mentioned above.

A rigorous discussion of double layer effects on kinetics has been given by Breiter, Kleinerman & Delahay (58), who also treat the double layer influence on coupled homogeneous chemical reactions. They have applied their ideas to the reduction of iodate ions and nitromethane using polarographic

techniques. Delahay & Kleinerman (59), working with thallium amalgams, have demonstrated that a change in zero point of charge shifts the current depression along the potential axis as the theory predicts. Gierst (56) has treated the same problem and has shown that one can use such double layer effects to analyze the mechanisms of electrode reactions. In particular he has demonstrated that the electrical charge of the reacting species can be assessed. The influence of double layer structure on kinetics, under conditions of specific adsorption of ions, appears in many investigations, especially those by the Russian workers (60, 60a, 61).

The influence of adsorption of neutral organic molecules on kinetics has been studied by Gierst (56), Lorenz (62), Delahay & Trachtenberg (63), and Laitinen & Subcasky (64). In a first approximation the inhibition of the electrode reaction can be explained by assuming that the reaction rate decreases linearly with surface coverage. The results of these authors with some redox reactions seem to show agreement with this assumption for medium coverage; but there are many indications that the adsorbed species very often have a chemical effect on the reacting species or on the transition state of the reaction, and that they can fundamentally change the kinetics in this manner.

Transport processes.—The theory of transport under natural convection conditions during stationary flow of current has been discussed again in its general aspects by Ibl (65, 65a), and for special cases by Tobias *et al.* (66) and Asada *et al.* (67). The last authors have also calculated limiting currents for the mercury jet electrode by means of rigorous hydrodynamic theory.

For the investigations of electrode processes under forced convection, two arrangements guarantee the highest homogeneity in the rate of transport to the whole surface: the expanding sphere and the rotating disc. The first arrangement is widely used in polarography, and the theory of transport under these conditions is well established. The versatility of the second arrangement has been emphasized especially by Frumkin and his school (see later discussion). The hydrodynamic theory for the rotating disc electrode has been somewhat improved from the original treatment of Levich by Gregory & Riddiford (68). An important new development is the Koutecky & Levich (69) calculation of limiting currents at the rotating disc electrode for conditions with a rate determination preceding homogeneous chemical reaction.

Semiconductor electrodes.—Although semiconducting materials (e.g., oxides) have been used in electrochemistry for a long time, the peculiarities in the electrode behaviour of semiconductors could not be recognized before the advent of high purity semiconductors such as germanium and silicon. That the electronic constitution of these materials can play an important role in electrode processes was shown initially by Brattain & Garrett in 1955 (70). Since that time this field has developed rapidly.

The theoretical aspects of electrode processes at semiconductors are discussed in close connection with semiconductor theory by Dewald (41) and Green (71). The differences between metal and semiconductor electrodes have been discussed by the author (72). Provided that no degeneration of electrons

or holes occurs in the surface, the influence of the applied voltage on the rate of charge transfer at a semiconductor is caused mainly by the accumulation or exhaustion in the surface of the mobile charge carriers, which are the free electrons in the conduction band and the holes in the valence band. The accumulation of holes in the surface accelerates, for example, the anodic dissolution of a semiconductor, because a hole, located at a surface atom, means that one of its chemical bonds to the crystal lattice is weakened to a great extent. As already mentioned in discussing electron transfer in redox reactions at semiconductor surfaces, one has to distinguish between electron transfer from and to the conduction band or from and to the valence band (41, 42). The latter process can also be described as exchange of holes. At semiconductors with a band gap greater than 0.4 v., normally only one of these processes will be observable with measurable rate, but the actual path for electron transfer depends on the redox system and the applied voltage.

Semiconductor-electrolyte interfaces can behave like rectifiers. For instance, a *p-n*-inversion layer can exist on the surface of an *n*-type semiconductor as a result of the accumulation of charge in the double layer. Current-voltage curves for such conditions have been discussed especially in analogy to the theory of *p-n*-junctions under current flow by Brattain & Garrett (70) and Vdovin, Levich & Miamlin (73). As with other *p-n*-junctions, large photoeffects indicate characteristically the presence of an inversion layer.

Another point of great theoretical interest is the influence of crystal orientation on the electrolytic behaviour of semiconductors. That there should be a large effect is obvious from a consideration of the number of bonds to next neighbours for surface atoms in different faces. In the diamond or wurtzite structure this number varies between one and three. Because a single bond in the semiconductor lattice is very strong, this means that great differences in reactivity of surface atoms on different faces should exist. This has been confirmed experimentally by Dewald (74) and by Gatos (75, 75a).

Passivity and protecting surface layers.—The theory of passivity of metals has lost a great deal of its "mysterious" character in the last two decades. Workers throughout the world have shown that passivity is caused by the formation of new surface compounds in at least a full monolayer, often much thicker, generally consisting of oxides. Some aspects of passivity have been summarized in a symposium (76) held in 1957 in memory of the late K. F. Bonhoeffer, one of the most successful initiators of the modern trends in passivity and electrochemical kinetics. Two reviews have appeared based on the papers given at this symposium (77, 77a). General aspects of passivity were discussed in this symposium by Evans (78), Uhlig (79), Hackerman (80), Vetter (81), Kolotyrkin (82), Huber (83), and Tomashov (84).

In general it can be stated that the problems of the growth of passive films have been confirmed as fully analogous to those of film growth during the oxidation of metals in contact with gases. However, the problem of the initiating condition for the first formation of a passive film, which has to occur in competition with the normal action of the active metal, still is not understood. This question has been discussed recently by Schwabe (85), who

came to the conclusion that the first stage of passivity is originated by a direct electrolytic oxidation of the surface, which results in the formation of a chemisorbed monolayer of oxygen.

Another important problem is how to develop a theory for the dissolution rate of the passive surface. Because all the passive films behave like semiconductors, the latter problem is closely related to the problems of the preceding section. This problem, which is further complicated by the highly specific action of various anions, seems at present to be the darkest point in our understanding of passivity. Experiments with pure metal oxides as electrodes, as carried out by Engell (86) for the oxides of iron, should be extended to other systems to help collect the details needed for a better insight into this question.

Non-oxide solid compounds formed on metal surfaces by electrolysis are very often porous. The kinetics of the formation of porous layers are very complicated and most of the kinetical discussions are highly formal. A review has been given by Jaenicke (87). This author has also done interesting experiments with silver salts on the kinetics of the dissolution of nonelectronic conducting salt films (88).

The phenomena of instabilities and oscillations at electrodes are closely related to the decay characteristic of current voltage curves in regions of conversion from the active to the passive state, as was shown earlier in the theoretical analysis of Bonhoeffer. This has been further analysed by Franck (89), who gives a generalized treatment for the origin of oscillations at electrodes with and without external currents.

EXPERIMENTAL METHODS

Single transient methods.—The theoretical discussions of current transients under potentiostatic conditions have been extended to complicated combinations of charge transfer with chemical or adsorption reactions. These calculations, done mainly by the Czechoslovakian school of Heyrovsky, have been in connection with polarography, where fully analogous problems arise and are complicated only by the expanding of the mercury drop. Some recent examples of such calculations can be found in papers by various authors (90 to 90e).

Application of the potentiostatic method for measuring the rate of preceding homogeneous reactions has been reported by Delahay & Oka (91) and Gerischer (92). Theoretical problems of the potentiostatic equipment with special regard to the regulating circuit speed and stability have been discussed [Fleischmann, Bewick & Liler (93), Gerischer & Staubach (94)].

An analogous situation is found for overvoltage transients under galvanostatic (also called amperostatic) conditions, where the transition time for more complex electrode reactions has been calculated by Dračka *et al.* (95, 95a). The influence of double layer structure on galvanostatic transients has been discussed by Gierst (96).

An improvement of the galvanostatic method, which compensates for the unfavourable relation between capacitive and faradaic current in the

initial part of the normal transient, has been developed in the double pulse method [Gerischer & Krause (97)]. This method uses a short but very high first pulse that mainly charges the double layer. The current is then reduced immediately to such a value that it just balances the faradaic current. This balancing condition is indicated by the electrode potential transient during these pulses. Matsuda *et al.* (98, 98a) have given a rigorous mathematical analysis of the polarization during such an experiment and have shown that varying the first pulse length permits an extrapolation to conditions of a first pulse with vanishing length. This allows measurement of the rate of charge transfer reactions without contributions of concentration polarization. These authors (98) have also discussed the influence of the diffuse double layer structure on this method, following the lines of Levich's discussion for ion transport in the diffuse double layer (see page 231).

An important application of this method to very fast electrode reactions in salt melts has been reported by Laitinen, Tischer & Roe (99).

Periodical, quasi-stationary methods.—The most generally applied method of this group is classical polarography. The periodicity is caused here by the dropping electrode.

A comprehensive review of polarographic theory and methodology has been given by Hume (100). Only a few special papers will be mentioned here besides those theoretical ones already quoted above in the discussion of potentiostatic transients (90).

The theory of transport processes under these conditions has been analyzed in a general form by Matsuda (101). Important developments in the analysis of polarographic limiting currents under more complex kinetic conditions, i.e. with proceeding or catalytic chemical reactions, have been reported by Koutecky, Koryta, and others (102, 102a, 102b). Brdicka (103) has reviewed these problems. A critical discussion of the interpretation of polarographic kinetical currents has been given by Becker & Strehlow (104) for the case of association-dissociation processes involving weak acids. The theory of Heyrovsky's oscillographic polarography has been improved in the papers of Gochstein & Gochstein (105).

The theory of electrode impedances under sinusoidal current flow today can be called a classical part of electrode kinetics. Matsuda (106), following the treatment of Levich for the transport processes in the diffuse double layer, recently discussed the corrections made necessary by the influence on the impedance of the electrical field in the diffuse double layer. A special case of the impedance, which arises from an earlier adsorption, was discussed by Llopis *et al.* (107). More difficult to understand are measurements with alternating current superimposed on direct current. The theory for this case has been reinvestigated by Matsuda (108) and Tamamushi & Tanaka (109).

A very important method for the investigation of very fast electrode reactions under equilibrium conditions has proved to be the faradaic rectification method, invented by Doss & Agarwal (110), and called by them redoxo-kinetic effect. The term faradaic rectification was proposed by Oldham (111) and characterizes the method very well.

The knowledge that this method can be applied to very fast electrode reactions when high frequencies in the Mc. region are used is attributable to Barker *et al.* (112, 112a), who have developed very effective equipment for this purpose and have also provided theoretical derivations. A very elegant derivation of the theory was published recently by Rangarajan (113). Matsuda & Delahay (114) have also discussed the theory of this method very rigorously and have included the influence of the double layer structure.

In this method the nonlinearities in the current-voltage relation, which are neglected in the normal impedance measurements as secondary effects, are used as characteristic parameters for the kinetics. As a result of any nonlinear component in the electrode current-voltage characteristic, a pure sinusoidal current will cause a small deviation of the mean steady-state potential from the equilibrium potential. The amount of this rectification voltage (and its sign) depends on the charge transfer coefficient α , which is the characteristic parameter for nonlinearities in the charge transfer reaction. It depends further on the exchange current density j_0 , and the characteristic diffusion terms for the transport of the components c_i that take part directly in the charge transfer reaction. These last terms are the same ones that control the contribution of concentration polarization to the impedance of the electrode.

The great advantage of this method is that a steady state is considered and the double layer capacity cancels so long as it does not significantly depend on electrode potential. In contrast to this, the double layer capacity is the predominant part in the normal impedance at high frequencies, and therefore limits the application of the usual a.c. methods to frequencies below 100 kc. Any potential dependence of the double layer capacity evidently also contributes to the rectification voltage.

The nonlinearities in the electrode characteristic simultaneously cause a faradaic distortion that means the appearance of harmonics in voltage and current. The first approach to a quantitative derivation of this effect seems to have been made by van Cakenberghe (115). His theoretical derivation does not include the contribution from transport processes (concentration polarization). The full theory of faradaic distortion has been derived recently by Oldham (116).

Application of an alternating square wave current or voltage (an extension of the respective single transient methods) has been reported by Wijnen & Smit (117), who have discussed the theory of this method for the quasi-stationary transients obtained in this case. The advantage of this method is that photographic recording can be avoided because a steady trace can be observed on an oscilloscope, but the accuracy obviously can only reach that of the single transient methods.

Periodical polarization with step function of the voltage is a method especially valuable for the detection of electroactive intermediates, or for the analysis of coupled chemical reactions. Examples of such possibilities have been given by Weber (118) and by Vlček (119).

Stationary convective methods.—Current voltage curves, under station-

ary convectional transport conditions for all the species involved in the electrode reaction, are the classical tools for the investigation of kinetics.

Randles (120) has compared the accuracy of data obtained this way with that from the a.c. method. A very general but formalistic representation for stationary current voltage curves with various coupled chemical reactions has been given by Riddiford (121). The effectiveness of the method for fast reactions depends on what rate of convectional transport can be attained. The rotating disc electrode, mentioned in an earlier section, is the most effective method in this respect. Interesting conclusions on coupling between charge transfer, transport processes, and chemical reactions can be obtained by studying the dependence of current voltage curves on the rotational frequency of the disc. An illustrative example of such possibilities has been given by Frumkin & Aikazyan (122). A brief review on the application of rotating electrodes can be found in a paper by Vielstich (123). The contribution of electrolytic migration in solutions containing little or no supporting electrolyte has been calculated by Yukhtanova (124).

Frumkin (125) has also introduced an ingenious modification of the rotating disc electrode that is suitable for detecting dissolved intermediates in electrode reactions. The modification uses a disc electrode with an auxiliary isolated ring around the periphery. This isolated ring can be polarized independently of the main disc. Soluble intermediates that are transported from the inner disc to the outer ring by the centrifugal streaming of the solution (with a high efficiency of about 40 per cent) can then be detected by electrolytic oxidation or reduction. This method has been applied by Frumkin *et al.* to the reduction of oxygen (126). The hydrodynamic theory of this method has been given by Ivanova & Levich (127).

Application of isotopes.—The usefulness of radioactive isotopes for the interpretation of electrode kinetics has been demonstrated in papers by Losev & Budov (128) who have investigated the ion transfer at amalgam reactions where the valency of the ions formed is higher than one. The special value of this method is that one can measure separately the net anodic and cathodic currents. This can provide criteria for deciding whether the charge is transferred in one step or in a series of one-electron steps. Horiuchi & Matsuda (129) have used the stoichiometric number to analyze the results obtained from such exchange measurements (130, 130a). Special complications arise for the tracer methods at solid electrodes due to the inhomogeneities of the surface (130, 130a). The high value of the oxygen isotope O^{18} for analyzing the mechanism of processes where oxygen is involved has been discussed by Frumkin (131).

INTERPRETATION OF KINETICS

DEPOSITION AND DISSOLUTION OF METALS WITHOUT FILM FORMATION

Liquid metals.—The rate of the Hg/Hg_2^{++} -exchange reaction in perchlorate solution has been measured with the double pulse method by Gerischer & Krause (97), and by Matsuda, Oka & Delahay (98). It was concluded from

the concentration dependence of the exchange current that no dissociation of the dimeric ion Hg_2^{++} occurred before discharge. For complex mercuric cyanide solutions, a discharge mechanism with preceding dissociation of the $[\text{Hg}(\text{CN})_4]^{--}$ complex and formation of an intermediate HgCN , adsorbed on the surface, has been formulated by Pérez-Fernández & Gerischer (132). Koryta (133) has treated in a general way the possibility of analyzing the mechanism of complex ion discharge process by means of polarographic methods. He has studied the discharge reactions of Cd^{++} , Mn^{++} , and Pb^{++} complexes with nitrilotriacetic acid (134, 134a) in this way and has shown that, in acid solutions, progressive dissociation of the complex can control the current in the first polarographic wave.

Another interesting case, studied by several authors (56, 92, 96, 135), is the discharge of $[\text{Cd}(\text{CN})_4]^{--}$ ions. Here again dissociation reactions play a decisive role. A similar situation has been found by Tanaka, Tamamushi & Kodama (136) for the cadmium-ethylenediamine-tetracetate complex. Matsuda & Ayabe (137) have studied the discharge of zinc complexes with hydroxyl ions and with ammonium. Gierst (56) has studied the reduction of $[\text{Ni}(\text{H}_2\text{O})_6]^{++}$ ion at a dropping mercury electrode and comes to the conclusion, from double layer structure considerations, that a slow dehydration should be the rate determining reaction step occurring in this process.

The interesting studies of Losev *et al.* (128) with radioactive tracers on the mechanism of the deposition of multivalent cations have been mentioned already. Vlček (138) has studied the reduction of cobalt and nickel complexes and has found unusual valence states for the intermediates. Losev & Molodov (139), studying the anodic dissolution rate of the Indium-amalgam electrode, have found a catalytic action of SO_4^{--} and the halogen anions. They interpret this as an effect of bridging between these anions and the reactants in the surface. The contrary effect, a depression in the cathodic reduction current of In^{++} ions in chloride solutions in the presence of some highly charged or surface active cations, has been found by Brainina (140). This can be explained by the Frumkin theory of double layer structure influence on kinetics.

Solid metals.—Only a very small difference in the exchange current density between solid and liquid mercury has been found by Gerischer & Krause (97), which shows that the crystallization process is rapid near the melting point. Under conditions far from the melting point, the crystallization process seems to be a slow step. This was confirmed in the case of silver by Gerischer *et al.* (52, 141), Mehl & Bockris (50), and Lorenz (51). Methods have been applied that allow calculation of the concentration of adsorbed silver atoms on the surface in equilibrium with the silver lattice (50, 51, 52). The author has given evidence for the partial ionic character of these adsorbed silver atoms (52). Highly theoretical calculations of the energy relations for the discharge of silver ions have been undertaken by Despič & Bockris (142).

The deposition of copper from Cu^{++} ionic solutions is more complicated,

but also here "ad-atoms" obviously play an important role for crystal growth or dissolution under low overvoltages. This has been demonstrated by Mattson & Bockris (143) and Fischer and co-workers (144). Lorenz, extending his measurements to lead, cadmium, and zinc, has achieved results for these systems similar to those for silver (51). Vermilyea *et al.* (145, 145a, 145b), in important experiments with copper and silver whiskers, have found that the crystal growth can also be a very fast process when the surface is atomically rough.

The surface structure of the metal obviously has an immense influence on the rate of crystallization. To compare the results of different experiments directly, therefore, is often rather questionable. It must be mentioned in this connection that all progress attained in this field will remain in a preliminary state until the surface structure of the electrode can be more carefully controlled.

Experiments with single crystals appear most promising in this respect. A series of such experiments has been reported by Piontelli, Poli, and co-workers (146 to 146c) for copper, lead, tin, and bismuth. Different crystal faces show different overvoltages. The anions, present in the solution, have a great influence on the overvoltage as has been emphasized for many years in the experiments of Piontelli. In some cases the order of overvoltage at a particular current density can be changed for different anions. The structural appearance of metal deposits of various metals showing dendrite growth, and in some cases on oriented crystal faces, has been studied by Wranglén (147).

A careful investigation, using electron microscope techniques, of the structure and orientation of copper deposits on single crystal faces has been performed by Pick *et al.* (148). At higher overvoltage, as used in these experiments, nucleation phenomena become very important. Intensive morphological studies on the structures of freshly formed crystals of electrodeposited copper have been reported by Seiter & Fischer (144). The application of electron microscope techniques to research on electrolytic deposits has been reviewed by Reimer (149), and a new technique for direct observation under the electron microscope has been developed by Wiesenberger (150).

The important question of how orientation of a single crystal affects the nucleation of new crystals on its surface has been treated by Kaishev and co-workers (151). In a very interesting paper on the deposition of silver onto a single crystal platinum sphere, they confirmed the theoretical calculations of Volmer on the relation between overvoltage and rate of nucleation.

The great influence of screw dislocations on electrocrystallization processes, postulated in the theory of Franck *et al.*, has been confirmed by the observation of spiral growth on silver and copper surfaces. Impressive examples of such spiral growth have been given by Kaishev and co-workers (152) and by Fischer and co-workers (144).

The question of how dislocations originate during crystal growth has been investigated very infrequently, but the present view is that during

electrodeposition these are formed mostly by the incorporation of impurities. Economou, Fischer & Trivich (153), in connection with some observations on copper, have discussed this problem and the question of how dislocations move and aggregate. Vermilyea (154) has found, for rapid whisker growth, a great reduction of the over-voltage that is necessary for nucleation onto copper. He attributes this to the incorporation of other atoms into the lattice during rapid crystal growth. An interesting investigation of copper deposits has been published by Steinemann & Hintermann (155) in which dislocations in the metal have been observed directly by transmission electron microscopy.

Although the electrolytic behaviour of the relatively noble metals is complicated enough, the situation is worse for the base metals. Progress in this field is slow, therefore, and one has to be content in most cases to discuss the phenomena in a rather formal manner, neglecting the details of crystal growth problems. Only a few papers will be mentioned here.

The mechanism of dissolution of iron has been discussed by Kabanov *et al.* (156, 156a), Bonhoeffer & Heusler (157, 157a), and Hoar *et al.* (158). A most interesting finding in this system is the catalytic action of hydroxyl ions, even in acid solutions.

A new mechanism for chromium deposition from chromic acid solutions has been proposed by Käppel & Gerischer (159). Some explanations for this problem, partially in conflict with the preceding paper, have been published by Vagramian & Usachev (160).

The question of monovalent ions as intermediates has been discussed for magnesium by Kabanov and co-workers (161) and by Straumanis (162). Monovalent beryllium intermediates in the anodic dissolution of this metal are indicated in the rotating ring disc experiments of Heusler (163).

A number of details of the anodic behaviour, mostly of less noble metals, can be found in a review article of Hoar (164).

Inhibition.—An extensive review of the problems of inhibition in crystal growth has been given recently by Fischer (165). Because most of the important examples can be found there, we shall mention only a very few papers. The metals investigated most frequently are nickel and copper. Electrolytic whisker growth seems to be closely related to inhibition, as concluded by Vermilyea *et al.* (145, 145a, 145b, 166) from their own experiments and from those of other authors (167, 167a).

Trivich *et al.* (168) have studied the influence of an inhibitor on the nucleation of new copper crystals at a copper single crystal sphere. They observed that the orienting influence of the crystal atomic array was suppressed in the presence of thiourea.

REDOX REACTIONS

Inorganic systems.—The theoretical progress in the treatment of redox reactions has already been discussed. From the experimental papers it may be mentioned that Randles (120) has studied the V^{++} — V^{+++} system and

Elving & Zemel (169) have investigated the reduction of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ ions with polarographic techniques. Vetter & Thiemke (170) have analyzed measurements on the $\text{Ti}^{3+}/\text{Ti}^+$ redox system in strong sulfuric acid solutions in terms of an intermediate formation of Ti^{2+} , which means a mechanism with two one-electron transfer reactions. Fischer & Dračka (171) have applied the galvanostatic method to the reduction of U (VI) to U (IV) where a disproportionation of the intermediate U (V) is accepted as being the rate determining step. They calculate from their measurements the rate constant for the disproportionation.

The reduction of $[\text{Ni}(\text{CN})_4]^{2-}$ at a mercury electrode results in the formation of $[\text{Ni}(\text{CN})_4]^{-1}$ as an intermediate, as Vlček (138) and Sartori, Furlani & Morpurgo (172) have demonstrated. This intermediate ion can be reoxidized in the solution and the resulting current increased in excess of the purely diffusional one.

Another rather complicated reaction is the electrolytic reduction of cobalt complexes containing ammonium and halogen ions, studied by Vlček & Kůta (173) and by Nikolaeva-Fedorovich & Frumkin (174). Cl^- ions catalyse this reduction reaction (Vlček) while tetraammonium ions act as inhibitors (Frumkin).

The mechanism of nitric acid reduction, analyzed already by Vetter, has been investigated by Schmid (175, 175a) with nonstationary methods to decide whether or not NO^+ takes part in the reaction mechanism.

Other interesting reactions studied are: sulfide and polysulfide oxidation [Hickling (176)]; reduction of dithionite and sulfite [Čermak (177)]; oxidation of sulfate to persulfate and anodic decomposition of ClO_4^- using isotopic methods [Gerovich & Kaganovich (178, 178a)]; reduction of chromic acid at a rotating disc electrode [Budevski & Toshev (179)]; and at a dropping mercury electrode [Gierst (56)]. The effects of double layer structure and anion or cation adsorption on persulfate reduction, and the reduction of other highly charged anions, have continued to be of interest in the papers of Frumkin *et al.* (180, 180a) and of Gierst (56) (as already mentioned).

Organic systems.—Reviews collecting a great deal of the polarographic experience of the electrode behaviour of organic molecules have been published by Wawzonek (181) and by Nürnberg (182). The distinction between aqueous and nonaqueous solutions cannot be maintained in this chapter because a great number of reactions can only be studied in mixtures of water with organic solvents to reach high enough solubility. A series of investigations, important because of correlation with theoretical concepts of reactivity, has been published by Hoijsink *et al.* (183 to 183d). Here the reduction of aromatic and conjugated hydrocarbons in various solvents is discussed. Aalbersberg & Mackor (184) have reported the polarographic reduction of cations of aromatic compounds that are formed in strong acid solutions by proton association.

The redox system, methyleneblue/leucomethyleneblue, has been investigated by Vetter & Bardeleben (185) and by Lorenz & Schmalz (186).

Valenta (187) has proposed a more detailed mechanism for the reduction of formaldehyde on the basis of new results obtained with an oscillographic technique. The reduction of substituted benzaldehydes has been studied very thoroughly by Grabovski *et al.* (188 to 188c), who in their interpretation also take into account the influence of double layer structure on the proton transfer of the reactants.

The mechanism of cathodic reduction of nitro- and nitroso-compounds has been followed in great detail by Holleck and co-workers (189, 189a), Martinyuk & Shlygin (190), and Kemula *et al.* (191). The reduction of hydroxylamine has been the subject of a paper by Grabovski & Zhdanov (192). Other investigations are concerned with: effect of negative substituents on reduction of carbon-halogenbonds [Mairanovskii *et al.* (193)]; reduction of phthalamide [Ryvolová (194)]; and the catalytic action of some cations on reduction of cystine [Březina (195)].

Oxidation reactions are studied much less frequently. The investigation by Ginzburg (196) on the oxidation of phenol at a platinum electrode and the papers of Bogdanovskii & Shlygin (197) on the oxidation of alcohols and aldehydes may be mentioned.

The mechanism of electrolytic hydrogenation of unsaturated compounds is an important and very interesting problem because there are so many close connections with catalytic hydrogenation. Such reactions at activated nickel electrodes have been studied by De Hemptinne & Jungers (198).

GAS ELECTRODES

Hydrogen electrode reaction.—The electrolytic evolution or oxidation of hydrogen has continued to remain one of the fascinating problems of electrode kinetics. A great number of investigations have been published during the period of this review. The general relations between strength of adsorption bond of the hydrogen atoms, the intermediate reaction products in every reaction path, and the mechanism and rate have been discussed again by Gerischer (199) and by Parsons (200). A similar discussion has been given by Krishtalik (201). Ives (202) has discussed the conditions for a reaction path with H_2^+ as intermediate, which is not taken into account in the discussions above. Such an intermediate was proposed many years ago by Horiuchi, who also rediscussed, with statistical mechanical methods, the possible reaction mechanisms (203, 203a).

An important new method for the investigation of this reaction has been introduced by Frumkin, Oshe, and Bagotskaja (204, 204a, b). The idea of this method is to supply additional hydrogen atoms to the surface at which the discharge of H^+ ions is studied, and to observe the influence of this additional atomic hydrogen on the overvoltage at constant current. Depending on which reaction step is rate determining, the overvoltage can increase or decrease. The additional H atoms were obtained by working with an iron membrane electrode that is permeable to hydrogen atoms generated electrolytically on the other side. In a similar arrangement, Oshe (205) has studied

the influence of surface active additives on the rate of diffusion of electro-lytically generated hydrogen atoms into an iron membrane.

Most of the papers are concerned with special electrode systems. Pentland, Bockris & Sheldon (206), using the steady state method, have studied the behaviour of several metals under conditions of high purity of the solutions. Details of hydrogen evolution reaction at platinum have been reported by Schuldiner (207), Parsons (208), and Kolotyrkin *et al.* (209).

The reversibility of the exchange between hydrogen ions and adsorbed hydrogen atoms at the platinum surface has been proved by Giner (210) and by Böld & Breiter (211). The latter authors also have measured the heat of adsorption of H atoms at different degrees of coverage. The anodic ionisation of H₂ molecules at platinum has been studied by Frumkin & Aikazyan (122), and the specific inhibition influence of some anions on this process has been investigated by Aikazyan (212) and Shanina (213). Other platinum metals such as palladium and rhodium have been studied by Schuldiner & Hoare (214, 214a, 214b). The adsorption of atomic hydrogen at rhodium and its dependence on pH has been followed by Tyurin (215), who has reported also that adsorption of one halogen ion displaces several H atoms from the surface. Palladium-platinum alloys as hydrogen electrodes have been studied by Carson, Flanagan & Lewis (216), and rhodium-palladium alloys by Hoare (217). The surface coverage of Ag electrodes with H atoms has been investigated by Devanathan, Bockris & Mehl (218).

Hydrogen overvoltages on oriented single crystals have been investigated at several metals (Pb, Sn, Ni, Cd, Bi, Cu) by Piontelli *et al.* (219, 219a, 219b), who have observed great differences at different faces. Christov & Pangarov (220) have compared the hydrogen overvoltage on the cubic and hexagonal modifications of chromium, which also behave very differently. Mitsuya & Sakai (221) have observed that the hydrogen overvoltage at an ordered Ni₃Mn alloy is about 60 mv. higher than at a disordered alloy of the same composition. The influence of the double layer structure and of specific ion adsorption on hydrogen overvoltage, which was first explained theoretically by Frumkin [compare (3)], has been studied for particular electrolyte solutions by Iofa *et al.* (222, 222a) and by Kolotyrkin (223). A number of organic compounds catalyse the hydrogen discharge at mercury. The constitutional conditions for this catalytic action have been studied by von Stackelberg and his co-workers (224, 224a, 224b).

Electrolytic separation of H, D, and T has been treated during this period in papers by von Stackelberg & Jahns (224c), and by Kodera & Saito (225).

Oxygen and halogen electrode reactions.—The mechanism of the oxygen evolution reaction is much more uncertain in its kinetic details than the hydrogen evolution mechanism. Apparently, one reason is that the net reaction here needs four electrons and therefore probably occurs in four steps; another is that in all cases oxide formation occurs in parallel, and what actually is studied is oxygen evolution on oxide surfaces. The mechanism of

electrolytic oxygen evolution, therefore, cannot be discussed independently of oxide formation. This has been shown for platinum by Laitinen & Enke (226), for nickel by Turian (227).

Rüetschi and co-workers (228) have studied the oxygen overvoltage at lead dioxide electrodes and have found a very different behaviour of the α - and β -PbO₂ modifications.

It is well known that the reduction of oxygen results in formation of H₂O₂ as a first relatively stable intermediate, as has been confirmed again by Frumkin (126) with the rotating ring disc technique. The oxidation of hydrogen peroxide to oxygen and its reverse therefore constitutes an important part of the oxygen electrode reaction. This step has been investigated at platinum by Giner (229); on C, Pt, Ni, and Ag by Vielstich (230); and on Pt, Au, Ag, and Hg by Akopyan (231).

Yeager *et al.* (232) have proved, using an isotopic technique with O¹⁸ as indicator, that the O—O bond in H₂O₂ is not broken during oxidation to O₂ at an activated carbon electrode.

The mechanism of the ionization of chlorine at the platinum electrode has been studied by Frumkin & Tedoradse (233) and the halogen systems, besides fluoride, at the platinum electrode by Llopis, Fernández-Biarge & Pérez-Fernández (234).

SEMICONDUCTOR ELECTRODES

The new aspects of semiconductor electrode theory have been considered previously. Most experimental investigations have been undertaken with germanium single crystals. Brattain & Garrett (70) were the first to observe, at an n-type germanium electrode, a saturation current limited only by the slow transfer of holes from the interior of the semiconductor to the surface. A detailed mechanism for the anodic dissolution of germanium has been deduced by Turner (235) and Beck & Gerischer (236). The anodic dissolution of germanium has been studied also by Efimov & Jerusalemchik (237). Complications arise from oxide formation on the surfaces of the semiconductors [e.g., Uhler (238), Turner (239), Schmidt & Michel (240)].

Flynn (241) also has found saturation currents for the anodic dissolution of n-type silicon in hydrofluoric acid. Saturation effects for the cathodic evolution of hydrogen have been observed by Brattain & Garrett (70) on p-type germanium, indicating that this reaction occurs via conductance electrons. These effects are obscured under stationary conditions [cf. Efimov & Jerusalemchik (242), or Erdélyi & Green (243), Green (71)] by the incorporation of hydrogen atoms into the surface region, or by hydride formation [Gerischer (244), Pleskov (245)].

The mechanism of hydrogen evolution at germanium has been discussed by Green and others (71, 234) and the writer (244). Measurements of the hydrogen overvoltage on silicon are reported by Efimov & Jerusalemchik (246), and by Seipt *et al.* (247, 247a).

The distinction between electrons or holes as reactants in electrode proc-

esses has needed the introduction of new techniques that are closely related to semiconductor research devices. In this respect, already Brattain & Garrett (70) have used, as Pleskov did later (248), a p - n -junction technique as the indicator for the charge carrier produced or consumed in an electrode reaction. Gerischer & Beck (42) have used variations in the saturation current at n -type germanium under anodic polarization as the indicator for processes that inject or extract holes in parallel with the anodic dissolution. Pleskov (245) has introduced a modification of the p - n -junction method, in which a thin slice of n -germanium, thinner than the mean free path of holes in this material, can be polarized independently at both sides in different electrolytic cells. When one side is polarized anodically into the saturation region, this arrangement can be used as an indicator for holes that diffuse through the slice from the other side. Furthermore, the effect of illumination can be used as an indicator for processes in which minority carriers are involved [Brattain & Garrett (70), Dewald (41, 249)].

As a result of a number of investigations with these methods, it has been proved that redox reactions of germanium follow either a valence band mechanism or a conductance band mechanism [Gerischer & Beck (42), Dewald (41), Pleskov (245, 250, 250a), Tomashov and co-workers (251), Efimov & Jerusalemchik (252)]. It has been shown that agreement with the theoretical expectations is found in most cases [Dewald (41), Gerischer (42, 72)].

The corrosion behaviour of such semiconductors has been studied in electrochemical aspect by Harvey, Gatos, and co-workers (253, 253a), Turner (254), Lovreček & Bockris (255), and Gerischer & Beck (256). Types of coupling (not found at metals) between anodic and cathodic processes are observed here when the minority carriers are unequally involved in the anodic and cathodic reaction.

Other semiconductors have been investigated far less, although very interesting results concerning the correlations between crystal structure and surface reactivity or other such properties are to be expected in this field. This has been indicated in the papers of Dewald (74) and Gatos and co-workers (75, 257) on the anodic or etching behaviour of such compound semiconductors as ZnO, InSb, GaAs, and other III-V-element compounds [see also Venables & Broudy (258)].

Among semiconductors with more complicated crystal structures, the electrode behaviour of selenium has been studied by Gobrecht, Kuhnkie & Tausend (259). Redox reactions at passivated steel surfaces, which can be assumed to be covered with a semiconducting oxide film, have been investigated by Stern and co-workers (260). The connection between passivity and semiconductor behaviour will certainly need further attention.

PASSIVITY AND FILM FORMATION ON ELECTRODES

Films with high electric conductivity.—The kinetics of anodic passivation of metals and the electrode behaviour of such film-covered surfaces have been studied intensively and continuously as mentioned previously. Some general

discussions of the thermodynamic properties of metal electrodes with films on their surface and of possible kinetic processes in such systems have been given by Göhr & Lange (261).

The passivity of iron is the problem most often studied in this field. The growth of the passive oxide film has been discussed by Vetter (81) and by Snavely & Hackerman (262), among others. Cohen (263) has studied the properties of passive films on iron.

The meaning of the critical potential that controls the change from the passive to the active state, the so called "Flade potential," has been discussed by Vetter (81), Weil (264), Göhr & Lange (265), Cartledge & Simpson (266), Uhlig & King (267), and Pryor (268). Although opinions differ greatly, it now seems to be most probable that this critical potential is determined by kinetic processes, and cannot be explained as a purely thermodynamical condition for passivity.

The formation of passivity on a continuously abraded iron surface has been studied by Schwabe (269). The important, but as yet unexplained, effect of halogen ions on the dissolution rate of passive iron has been investigated by Cohen *et al.* (270), Weil & Menzel (271), and Engell & Stolica (272).

Passivity on nickel has been studied by Okamoto *et al.* (273), Schwabe *et al.* (274), Piontelli *et al.* (275, 275a), Vetter & Arnold (276), and Kolotyркиn *et al.* (277); the passivity of chromium by Kolotyркиn *et al.* (278, 278a), Weidinger & Lange (279), and Heumann *et al.* (280). For a long time interest has centred on oxide systems used in batteries, such as silver/silveroxide [Lange *et al.* (281, 281a), Kabanov *et al.* (282, 282a), Rüetschi *et al.* (283), Wales & Burbank (284)] or lead/lead-dioxide [Rüetschi *et al.* (285), Fleischmann *et al.* (286, 286a)]. The formation of oxide layers on platinum, palladium, and gold has been followed by means of charging curves by Vetter and Berndt (287).

The list of such investigations, including the papers concerning alloy behaviour, could be extended almost indefinitely and is beyond the scope of this review.

Films with low electric conductivity.—Growth of such films, which are very poor electron conductors, is controlled in most cases by cation migration under the strong electric fields that are present under anodic polarisation. The classical and best investigated examples are tantalum and aluminum, where the anodic growth of thicker oxide layers can be described in principle by the old theory of Güntherschulze & Betz (288). Going into more details, complications arise [compare the review of Young (289)] from space charge contribution to the electric field in the oxides [Vermilyea (290), Young *et al.* (291), van Geel *et al.* (292)] and from field effects on the concentration of defects in the oxides, as manifested in transient experiments by Vermilyea (293) and Young (294). The high field can also help to form nuclei for crystallization of the initially amorphous oxide on tantalum [Vermilyea (295)], and aluminum [Stirland & Bicknell (296)]. Another interesting effect, observed by Vermilyea (297) and Young *et al.* (297a), is the acceleration of growth

rate under illumination with ultraviolet light. A paper by Byalobzheskiĭ & Val'kov (298) on the influence of illumination on electrode behaviour of a number of metals coated with their oxides as films should also be mentioned here.

The electrode behaviour of various metals (Al, Hf, Nb, Ta, Ti, Zr, and others) with very thin films has been studied by Adams *et al.* (299 to 299c). An interesting paper on the anodic dissolution of molybdenum and tungsten has been published by Besson & Drautzburg (300), who find strong linear Tafel relations for the oxidation of these metals to MoO_4^{--} or WO_4^{--} anions in alkaline solutions, similar to the anodic behaviour of chromium. The effects of alloying more noble elements to these above-mentioned metals are very important, and have been studied from the corrosion point of view, for example, by Tomashov (301) and by Stern & Wissenberg (302).

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MOLECULAR ELECTRONIC SPECTROSCOPY¹

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INTRODUCTION

The purpose of this review is to give an overall picture of developments during the past year, with some emphasis on high resolution studies of simple molecules. Important advances have been made in recent years in our understanding of the electronic spectra of small polyatomic molecules; but a detailed discussion will not be given here, as the author (348) has recently completed an extensive review of this subject. Instead, a brief summary will be included here. Other discussions of this field have been given by Herzberg (172, 173, 174), Mulliken (294), and Walsh (412).

The bibliography is based on papers listed in Current Chemical Papers between November 1959 and November 1960 inclusive. Occasionally other papers are included. Since the initial survey produced more than 600 papers, selectivity was necessary. Papers containing spectra with no interpretation have been omitted, and the selection of papers of purely theoretical interest may be far from complete. If important papers have been inadvertently overlooked, the author extends a sincere apology.

Reviews that have appeared during the last year or are currently in press include: "The Electronic Spectra of Simple Polyatomic Molecules" by Herzberg (174), "The Triplet State in Chemistry" by Porter (343), "The Spectra of Polyatomic Free Radicals" by Ramsay (346), "Molecular Electronic Spectroscopy" by Robinson (362) and "Molecular Spectra in the Vacuum Ultraviolet" by Wilkinson (422). In addition a *Bibliography of the Spectra of Diatomic Molecules 1950-1960* has been prepared by Herzberg & Howe (175). A useful survey of the development of theoretical calculations is afforded by the proceedings of the Boulder Conference on Molecular Quantum Mechanics (326).

DIATOMIC MOLECULES

THEORETICAL

Molecular orbital and valence bond calculations have been carried out for He_2^+ [Csavinszky (83)], LiH^+ [Platas, Hurst & Matsen (339)], LiH [Karo (217), Moccia (282), Robinson, Stuart & Matsen (365)], BeH^+ [Moccia (282)], NH [Companion & Ellison (73)], HF [Karo & Allen (218)], C_2 [Clementi & Pitzer (71)], CO [Brion & Moser (46)], and O_2^- [Mulliken (295)]. To facilitate the comparison of theory and experiment, potential energy curves have been calculated from spectroscopic data by Vanderslice, Mason, Lippincott, Fallon and Maisch using the Rydberg-Klein-Rees method for LiH (125), HF (124), N_2 (402), NO (403), and O_2 (404). It is in-

¹ The survey of literature pertaining to this review was concluded in November 1960.

teresting to note that the dipole moment of LiH has recently been measured by Wharton, Gold & Klemperer (418) and the value obtained ($\mu = 5.882 \pm 0.003D$) agrees well with the predictions of theory ($\mu = 5.5 - 6.5D$).

Kovács has carried out investigations of the multiplet splittings in several molecules. He has shown that the anomalous multiplet splitting in the ${}^2\Sigma$ state of MnH (233) may be attributed to perturbation by a neighbouring ${}^2\Pi$ state. The anomalies found in the ${}^4\Pi$ state of O_2^+ (232) may be attributed to perturbation by the two known ${}^2\Pi$ states, to spin-spin interaction, or to both of these effects. In a similar manner the deviations of the rotational term values of the A ${}^3\Pi$ state of NH (234) from the well-known formulae may be attributed to perturbation by a ${}^1\Pi$ state and to spin-spin interaction. Kovács (235) has also obtained theoretical expressions for the intensity distributions in the branches of the forbidden transitions ${}^1\Sigma - {}^3\Delta$, ${}^3\Sigma - {}^3\Delta$ and ${}^1\Pi - {}^3\Delta$.

ROTATIONAL AND VIBRATIONAL ANALYSES

Homonuclear molecules.—The far ultraviolet absorption spectra of H_2 , HD, and D_2 in the region of 850 Å have been investigated by Herzberg & Monfils (177) under high resolution and more accurate values for the dissociation energies determined [$D_0^0(H_2) = 36113.0 \pm 0.3$ cm. $^{-1}$, $D_0^0(HD) = 36399.9 \pm 1.0$ cm. $^{-1}$, $D_0^0(D_2) = 36743.6 \pm 0.5$ cm. $^{-1}$]. Independent values for D_e have also been determined for the three molecules. A slight difference (2.7 ± 0.8 cm. $^{-1}$) between $D_e(H_2)$ and $D_e(D_2)$ has been found and ascribed to an electronic isotope effect.

A new band system of the C_2 molecule in the near infrared region (3800 to 8600 cm. $^{-1}$) has been found by Ballik & Ramsay (22) in emission from a carbon furnace. The bands are due to an $A' {}^3\Sigma_g^- - (X) {}^3\Pi_u$ transition and the molecular constants of the ${}^3\Sigma_g^-$ state have recently been determined. Some small perturbations (~ 0.2 cm. $^{-1}$) in the rotational energy levels of the $A' {}^3\Sigma_g^-$ state were observed and the equal and opposite perturbations were found in the levels of the $a {}^1\Sigma_g^+$ state from new measurements of the Phillips system ($b {}^1\Pi_u - a {}^1\Sigma_g^+$). From these mutual perturbations it was deduced that the $a {}^1\Sigma_g^+$ state is the true ground state of the C_2 molecule and lies 610 ± 10 cm. $^{-1}$ below the $(X) {}^3\Pi_u$ state, which was formerly believed to be the ground state.

A new forbidden band system of nitrogen in the vacuum ultraviolet region has been identified by Wilkinson (421) and assigned to the transition $B' {}^3\Sigma_u^- \leftarrow X {}^1\Sigma_g^+$. The bands consist of an unresolved Q branch (qQ , qP , and qR) and sR and oP branches. Rotational and vibrational constants are given for the new $B' {}^3\Sigma_u^-$ state. This state has recently been shown by Carroll & Rubalcava (62, 63) and Dieke & Heath (100) to be the upper state of some near infrared bands of nitrogen, known as the Y -bands. These bands are due to the transition $B' {}^3\Sigma_u^- - B {}^3\Pi_g$. A rotational analysis of the 5-1 band has been reported by the former authors and of another band (probably the 8-3) by the latter authors.

A detailed investigation of the ultraviolet resonance spectrum of iodine has been carried out by Verma (409). The ground state vibrational intervals have been obtained from $v''=0$ to the dissociation limit ($v''=115$) and a more accurate value obtained for the dissociation energy, viz. $D_0(I_2) = 12452.5 \pm 1.5 \text{ cm}^{-1}$. The potential energy curve for the ground state has been calculated and certain curious features in the neighbourhood of the dissociation limit noted.

The $C-X$ and $D-X$ systems of Li_2 and Na_2 have been studied in absorption under high resolution by Barrow, Travis & Wright (30) and shown to be due to ${}^1\Pi_u - {}^1\Sigma_g^+$ transitions. Rotational and vibrational constants are given for the excited states.

Hydrides.—Rotational analyses have been carried out for the (0-0) and (1-0) bands of the $A {}^1\Pi_t - X {}^2\Sigma^-$ transition of NH [Dixon (102), Guenebaut & Pannetier (163)] and also for the (0-0) band of the corresponding transition for ND [Pannetier, Guenebaut & Hajal (322)]. A similar analysis has been carried out for the (1-0) band of PH [Legay (244)].

The (2-0) bands of the $A {}^2\Sigma^+ - X {}^2\Pi$ system of SH and SD have been analysed by Johns & Ramsay (209) and vibrational constants obtained for the $A {}^2\Sigma^+$ state. A more reliable estimate of the ground state dissociation energy has been deduced, viz. $D_0(SH) = 28,400 \pm 1000 \text{ cm}^{-1}$.

The $A {}^1\Pi - X {}^1\Sigma$ system of CH^+ has been extended by Douglas & Morton (109) and large perturbations found in the $v'=3$ and 4 levels. These results cast some doubt on the previously accepted values for the dissociation energy of CH^+ and the ionisation potential of CH. The hitherto unidentified interstellar line $\lambda 3579$ was identified as the R(0) line of the (3-0) band of CH^+ .

Oxides.—Rotational analyses of several of the "methyl iodide flame bands" by Durie, Legay & Ramsay (114) have confirmed the earlier assignments of these bands to the IO molecule. Lakshman (242) has given a rotational analysis for the (0-0) band of the $B {}^2\Sigma - X {}^2\Pi$ system of SbO and also reports a new $C {}^2\Delta_r - X {}^2\Pi_r$ band system for this molecule. In collaboration with Rao (243), he reports two new doublet systems which are assigned to $C-X$ and $D-X$ transitions of AsO, and a new singlet system which is assigned to AsO^+ . A rotational analysis of the TiO band near 11032 Å by Pettersson (336) shows that it is the (0-0) band of a ${}^1\Pi - {}^1\Sigma$ transition, which has the upper state in common with the ${}^1\Pi - {}^1\Delta$ band near 8860 Å. Rotational analyses for the $B {}^2\Sigma - X {}^2\Sigma$ and $A {}^2\Pi_r - X {}^2\Sigma$ systems of YO have been carried out by Uhler & Åkerlind (401) while the vibrational analysis of the $A-X$ system of MnO has been extended by Sarma (369). Vibrational assignments for eight transitions of LaO are discussed by Hautecler & Rosen (167).

Halides.—Rotational and vibrational analyses have been carried out for bands of the $B {}^2\Sigma - X {}^2\Pi$ system of SiCl [Ovcharenko, Tunitskii & Yakutin (316)], the $C {}^2\Pi_r - X {}^2\Sigma^+$ system of CaCl [Morgan & Barrow (289)] and the $B {}^3\Pi_0^+ - X {}^1\Sigma^+$ systems of AgCl and AgI [Barrow, Morgan & Wright (29)]. Molecular constants for InCl have been obtained by Younger & Winans (429) from rotational analysis of the (0-0), (0-1), and (1-0) bands of the

A ${}^3\Pi_0^+ - X\ {}^1\Sigma^+$ system in absorption. The magnetic rotation spectra of ICl and IBr have been studied by Eberhardt, Cheng & Renner (118) and were found to provide classic examples of the theory of the phenomenon.

Vibrational analyses have been given by Wieland (419) for the $B\ {}^3\Sigma^+ - X\ {}^3\Sigma^+$ systems of HgBr and HgI and estimates for the dissociation energies reported. Revised values for dissociation energies have been given by Novikov & Tunitskii (310) for BeCl and by Venkateswarlu & Khanna (408) for BiCl. These new values are based on extensions of well-known band systems to higher vibrational quantum numbers. Reddy & Rao (354, 355) have reported vibrational analyses for four band systems of FeCl, nine band systems of NiCl, and six band systems of NiBr. The spectra were excited in high frequency and heavy current discharges.

Others.—A new band system has been observed by McKinney & Innes (275) in emission from a King furnace containing aluminum, sulfur and argon at 1800°C. The bands are assigned to an $A\ {}^3\Sigma^+ - X\ {}^3\Sigma^+$ transition of AIS and rotational and vibrational constants are given. Further work has been carried out on the emission and absorption spectrum of PbTe by Grove & Ginsburg (161). A new band system of AuMg has been reported by Schiltz (370).

Thrush (390) has obtained absorption spectra of BCl, BH, BN, BO, SiCl, SiH, and SiN using a flash discharge technique [cf. Nelson & Ramsay (304)]. Since the triplet but not the singlet bands of BN were observed in absorption, Thrush suggests that the ${}^3\Pi$ state may be the ground state of BN in contrast to the result obtained for the isoelectronic molecule C_2 (see above). For BeO, however, Thrush (391) finds that a ${}^1\Sigma^+$ state is the ground state of the molecule.

Two interesting new bands in the regions 5507 to 5120 Å and 5081 to 4960 Å have been reported by Jongerius, van Koevinge & Oskam (211) in emission from discharges through a 50-50 mixture of argon and xenon. These bands do not appear in discharges through pure argon or xenon and are tentatively attributed to an AXe molecule or ion. Similar investigations of krypton-xenon bands in the visible region have been carried out by Friedl (142).

INTENSITIES

The radiative lifetimes of the $A\ {}^3\Delta$ and $B\ {}^3\Sigma$ states of CH and the $A\ {}^3\Pi$ state of NH have been measured by Bennett & Dalby (33) and found to be $(5.6 \pm 0.6)10^{-7}$, $(1.0 \pm 0.4)10^{-8}$ and $(4.25 \pm 0.6)10^{-7}$ sec. respectively. The oscillator strengths of the respective ground state transitions are $(4.9 \pm 0.5)10^{-3}$, $(1.2 \pm 0.4)10^{-3}$ and $(8.0 \pm 1.1)10^{-3}$. Similar measurements by these authors (32) for the comet-tail system of CO^+ ($A\ {}^3\Pi - X\ {}^3\Sigma$) yield $\tau \sim 2.6 \times 10^{-8}$ sec. and $f = (2.2 \pm 0.5)10^{-3}$; an appreciable variation (about 50 per cent) of τ with the upper state vibrational quantum number was noted.

The f -value for the $A\ {}^3\Sigma^+ - X\ {}^3\Pi$ transition of OH has been determined by Carrington (61) using a curve of growth method; his value $(11.7 \pm 4)10^{-4}$

corresponds to a radiative lifetime of 5.5×10^{-7} sec. for the $A \ ^2\Sigma^+$ state. The profiles of the lines of the $B \ ^2\Sigma^- - X \ ^2\Pi$ bands of CH emitted by an oxy-acetylene flame have been studied by James (204) using a quartz Littrow spectrograph and a Fabry-Perot etalon. The widths and shapes of the lines were attributed to a combination of Doppler broadening with a Gaussian profile, and collision broadening with a Lorentz profile. A collision diameter ~ 4 Å was assumed.

Franck-Condon factors have been calculated by Nicholls *et al.* (306) for the following molecular transitions: BeO, $B \ ^1\Sigma^+ - X \ ^1\Sigma^+$; BO, $A \ ^3\Pi_i - X \ ^2\Sigma^+$; CH⁺, $A \ ^1\Pi - X \ ^1\Sigma^+$; CO, $B \ ^1\Sigma^+ - A \ ^1\Pi$ and $b \ ^2\Sigma^+ - a \ ^2\Pi_r$; NO, $B \ ^2\Pi_r - X \ ^2\Pi$; SH and SD, $A \ ^2\Sigma^+ - X \ ^2\Pi_i$; O₂, $a \ ^1\Delta_g - X \ ^3\Sigma_g^-$; O₂⁺, $A \ ^2\Pi_u - X \ ^2\Pi_g$. Similar calculations have been carried out by Jarman, Ebisuzaki & Nicholls (206) for the fourth positive bands of CO and by Pillow & Rowlatt (337) for the triplet system ($d \ ^2\Pi - a \ ^2\Pi$) of this molecule. An approximate method for calculating Franck-Condon factors when v is large has been discussed by Biberman & Yakubov (37).

Relative band intensities for the $A \ ^2\Pi_i - X \ ^2\Sigma^+$ system of CO⁺ and the $A \ ^2\Pi_i - X \ ^2\Sigma^+$ and $B \ ^2\Sigma^+ - X \ ^2\Sigma^+$ systems of BO have been measured photoelectrically by Robinson & Nicholls (361) and the results used to determine the variation of the electronic transition moment $R_e(r)$ with the internuclear distance r . Similar investigations were carried out by Tawde & Murthy (389) for the $B \ ^1\Sigma^+ - X \ ^1\Sigma^+$ bands of BeO and by Erkovich & Pisarevsky (122) for the $A \ ^2\Sigma - X \ ^2\Pi$ and $B \ ^2\Pi - X \ ^2\Pi$ bands of NO.

The vibrational intensity distribution of the first positive bands of nitrogen ($B \ ^3\Pi - A \ ^3\Sigma$) in the nitrogen afterglow has been studied by Kurzweg & Broida (241) as a function of pressure, flow rate, diluent, and temperature. The measurements cannot be reconciled with the generally accepted, preassociation mechanism for the afterglow. Kishko & Kuchinka (223) have investigated the intensities of the second positive bands of nitrogen ($C \ ^2\Pi - B \ ^2\Pi$) as a function of the energy of the exciting electrons, while Reeves, Nicholls & Bromley (356) have studied the optical excitation of nitrogen using high energy (0.5–1.5 Mev) H⁺, H₂⁺ and H₃⁺ particles.

Intensity measurements of the components of rotationally perturbed lines in the (0-0) band of the violet system ($B \ ^2\Sigma^+ - X \ ^2\Sigma^+$) of CN, formed in an active nitrogen flame, have been made by Broida & Golden (49) over a wide pressure range. A simple kinetic model is advanced to explain the observed variations in the intensity ratios of the *main* and *extra* lines.

PREDISSOCIATION

A new predissociation in the nitrogen molecule has been reported by Lofthus (253) who finds a breaking-off in the vibrational and rotational structure above $v' = 2$, $J' \sim 15$ in bands of the $x \ ^1\Sigma_g^- - a' \ ^1\Sigma_u^-$ system. He attributes the predissociation to a $^2\Sigma_g^-$ and/or a $^3\Pi_g$ state formed from N(²D) + N(²D).

Deézi (92) has published a new value for the dissociation energy of

NO, viz. $D_0(\text{NO}) = 6.603$ eV, which is slightly higher than the accepted value of 6.50 eV. Her result is based on the breaking-off in the rotational structure of the γ -bands. From her limiting curve of predissociation however it is clear that the value of 6.603 eV represents an upper limit rather than a definitive value for the dissociation energy. From her data one can infer that the upper state has a potential maximum in the region of 2.3 Å. Deézi (93) has also identified three emission bands of the β -system involving the $v' = 7$ level, which lies just below the predissociation limit.

Some neglected cases of predissociation in diatomic molecules have been discussed by Mulliken (296), special emphasis being devoted to cases in which the potential energy curve for the predissociating state crosses that of the predissociated state at an internuclear distance less than the equilibrium distance of the latter state. Some probable examples are considered.

SIMPLE POLYATOMIC MOLECULES

THEORETICAL

Molecular orbital calculations have been carried out for CH_2 and CH_3 [Padgett & Krauss (317)], NH_3^+ [Lorquet & Lefebvre-Brion (256)], FHF^- [Bessis & Bratož (36)], C_2H_2 [King (222), Burnelle (55)], CO_2 and C_2H_2 [McLean (276), McLean, Ransil & Mulliken (277)], H_2CO [Parks & Parr (328)], NO_2 and CH_3NO_2 [McEwen (273)] and CH_2NO_2^- [Nagakura (302)]. Pitzer & Clementi (338) have carried out calculations on carbon vapor and find that the odd species C_3 , C_5 , ... should be relatively more stable than the even species C_2 , C_4 , ...

Albrecht (8) has investigated the influence of vibrational motions on the intensities of the forbidden $B_{2u} - A_{1g}$, $B_{1u} - A_{1g}$ and $E_{2g} - A_{1g}$ transitions in benzene and has considered the possible effects of isotopic substitution on the forbidden intensities. He has also made calculations on the intensities of "forbidden" bands in allowed electronic transitions (7) and has applied his theory to certain *p*-disubstituted benzenes.

HIGH RESOLUTION STUDIES

Considerable advances have been made in the last few years in our understanding of the electronic spectra of simple polyatomic molecules. High resolution studies have provided detailed information concerning the excited states of many molecules and have yielded accurate determinations of molecular constants. It is now well established that a considerable change in the geometry of the molecule often accompanies an electronic transition. A recent example of this phenomenon is afforded by the analysis of the 1600 Å band system of ammonia [Douglas & Hollas (108)] which shows that the molecule undergoes a transition from a pyramidal configuration in the ground state to a planar configuration in the upper state.

It is worthwhile at this stage to summarize the molecules for which rotational analyses have been carried out. These are: CH_2 [Herzberg & Shoomsmith (179), Herzberg (174)], NH_2 and ND_2 [Dressler & Ramsay (112),

Eaton, Johns & Ramsay (116)], HCN and DCN [Herzberg & Innes (176)], HCO and DCO [Herzberg & Ramsay (178), Johns & Ramsay (208)], HNO and DNO [Dalby (89), Clement & Ramsay (70)], C_3 [Douglas (107), Kiess & Broida (220)], $^{13}C_3$ [Clusius & Douglas (72)], NCO [Dixon (104, 105)], NCS [Dixon & Ramsay (106)], BO_2 [Johns (207)], CO_2^+ [Bueso-Sanllehi (54), Mrozowski (292)], CS_2^+ [Callomon (57)], N_2O^+ [Callomon (58)], CS_2 [Liebermann (248), Kleman (225)], CH_3 and CD_3 [Herzberg (174)], NH_3 [Douglas & Hollas (108)], C_2H_2 and C_2D_2 [Ingold & King (189), Innes (190)], H_2CO and D_2CO [Dieke & Kistiakowsky (99), Dyne (115), Robinson & DiGiorgio (363), DiGiorgio & Robinson (101)], FHCN and FDCN [Giddings & Innes (146)], $C_4H_2^+$ and $C_4D_2^+$ [Callomon (56)], $C_2H_2O_2$ (glyoxal) and $C_2D_2O_2$ [King (221)], the three isomeric diazines, viz. pyridazine (1:2), pyrimidine (1:3) and pyrazine (1:4) [Innes *et al.* (191, 279, 280, 392)], and *sym*-tetrazine [Mason (266)].

Since Herzberg (172) has discussed some of these molecules in his 1957 review, only the more recent work will be considered here. Two transitions of the CH_2 radical have been observed in absorption during flash photolysis experiments with diazomethane by Herzberg *et al.* (174, 179). The first system lies in the vacuum ultraviolet near 1400 Å and consists of a few bands that are diffuse because of predissociation of the molecule in the excited state. For CHD and CD_2 , however, the strongest bands exhibit rotational fine structures, although the lines are still distinctly broad. The bands have the appearance of a $\Sigma-\Sigma$ transition of a linear molecule and an alternation in the intensities of successive rotational lines is observed for CD_2 but not for CHD. From the rotational analysis, assuming a linear configuration for the molecule in both states, the following bond lengths are obtained: for CHD r_0'' (CH) = r_0'' (CD) = 1.034 Å, r_0' (CH) = r_0' (CD) = 1.090 Å; for CD_2 r_0'' (CD) = 1.029 Å, r_0' = 1.079 Å. It may be noted that the CH (or CD) bond in the lower state is the shortest CH bond yet known. The transition probably involves the lowest triplet state of the molecule viz. $^3\Sigma_g^-$, and an excited $^3\Sigma_u^-$ state which is probably a Rydberg state of the molecule with $n=3$.

The other transition of the CH_2 radical lies in the region from 6000 to 9000 Å. The bands are similar to the well-known α -bands of NH_3 , and may be assigned to the transition $^1B_1 \leftarrow ^1A_1$. The molecule has a bent configuration in the lower state and a linear configuration in the excited state. Both states correlate with a $^1\Delta_g$ state in the linear configuration. It is not yet certain whether the 1A_1 or the $^3\Sigma_g^-$ state is the true ground state of the molecule, though experiments in which a considerable excess of inert gas is added to the diazomethane strongly favor the $^3\Sigma_g^-$ state as the ground state.

The earlier analysis [Dressler & Ramsay (112)] of the α -bands of NH_3 and ND_3 has been extended by Eaton, Johns & Ramsay (116) with particular emphasis on the long wavelength region. This molecule provided the first example of the Renner effect (see below), and the vibronic structure of the levels is of particular interest. Altogether, 56 vibronic levels of NH_3 and 47 vibronic levels of ND_3 have now been identified.

Further work has been carried out on the HCO and HNO molecules. Spokes & Gaydon (380) have studied the hydrocarbon flame bands in emission from acetylene-oxygen flames, using deuterated, non-deuterated, and partly deuterated samples of acetylene, and have shown conclusively that the emitter contains only one H (or D) atom. The assignment to HCO is therefore very plausible. The absorption system of HCO and DCO in the region 4500 to 7500 Å, which was studied earlier by Herzberg & Ramsay (178), has recently been extended by Johns & Ramsay (208). Further vibrational levels have been found for both the ground and excited states.

An interesting case of predissociation has been found in the emission spectrum of HNO and DNO by Clement & Ramsay (70). The bands were excited by the reaction of H (or D) atoms with NO, and a sharp breaking-off in the *K*-rotational structures of the bands, due to predissociation of the molecule in the excited state, was observed for two bands of HNO and three bands of DNO. From the energies of the predissociation limits it was found that $D_0(\text{HNO}) \leq 17,000 \text{ cm}^{-1}$ and $D_0(\text{DNO}) \leq 17,190 \text{ cm}^{-1}$. The predissociation limit for HNO has been confirmed by the observation of diffuseness of some of the rotational lines in the absorption spectrum [Hollas & Ramsay (Unpublished)].

Six molecules (NCO, NCS, BO_2 , CO_2^+ , CS_2^+ , and N_2O^+) in the general class of AB_2 or ABC molecules with 15 valency electrons have now been studied under high resolution. All these molecules have $^2\Pi_{(g)}$ ground states and are linear. The first two excited states are $^2\Sigma_{(u)}^+$ and $^2\Pi_{(u)}$ states in which the molecules are also linear. The work on CO_2^+ was carried out at Chicago (54, 292) in the 1940's, but work on the other molecules is comparatively recent. The transitions $A \ ^2\Sigma^+ - X \ ^2\Pi_i$ and $B \ ^2\Pi - X \ ^2\Pi_i$ for NCO have been studied by Dixon (104, 105) in absorption and found to have the characteristics of linear-linear transitions. All the vibrational frequencies and first order anharmonic constants were obtained for the $A \ ^2\Sigma^+$ state and were found to be remarkably similar to the corresponding constants for CO_2 in its $X \ ^1\Sigma_g^+$ ground state. As in CO_2 , a Fermi resonance between ν_1' and $2\nu_2'$ was also observed. Anomalous band intensities were found for some of the combination bands in Fermi resonance and are discussed in another paper by Dixon (103). The $^2\Pi - ^2\Pi$ transitions of NCS [Dixon & Ramsay (106)] and BO_2 [Johns (207)] have also been studied in absorption, while the $^2\Sigma^+ - ^2\Pi$ transitions of CS_2^+ and N_2O^+ have been investigated in emission by Callomon (57, 58). For all these molecules it is found that the *B* values for the molecules in the excited states are very similar (± 8 per cent) to those for the ground states.

Tanaka, Jursa & LeBlanc (388) have studied the absorption spectra of CO_2 , CS_2 , COS, and N_2O in the vacuum ultraviolet down to 500 Å and have found Rydberg series leading to the first and higher ionisation limits. Two limits were found for CO_2 , three for COS and N_2O and four for CS_2 . Since the energies of some of the excited states of CO_2^+ , N_2O^+ , and CS_2^+ are known (see last paragraph), the states of the ion corresponding to some of the

higher ionisation limits of CO_2 , N_2O , and CS_2 may be unambiguously determined.

Rotational analysis of the bands of the 1600 Å system of NH_3 by Douglas & Hollas (108) has revealed that the molecule has a planar configuration in the excited state. The bands form a progression of the out-of-plane bending vibration ν_2' , where $\nu_2' = 0, 1, \dots, 8$. The bands are of the perpendicular type, indicating that the upper state is a ${}^1E''$ electronic state. Although a very large ℓ -type doubling has been found for the $K=1$ rotational levels in the upper state, the authors find no evidence for the existence of a Jahn-Teller effect. Walsh & Warsop (413) have carried out a more extensive investigation of the ultraviolet absorption spectrum of ammonia and the deutero-ammonias, though at lower resolution. They find a Rydberg series leading to an ionisation limit at 10.1 eV, the first three members of the series having origins at 2168 Å, 1434 Å, and 1330 Å, respectively. Each transition consists principally of a progression involving the bending vibration in the excited state; from this the authors deduce that the molecule has a planar configuration in each of the excited states and also in the ground state of the ion.

The near ultraviolet spectra of FHCO and FDCO have been investigated under high resolution by Giddings & Innes (146). From the vibrational analysis of the spectra, together with the rotational analysis of four bands, the authors conclude that the molecule has a non-planar structure in the excited state and the C—O bond is 0.18 Å longer than in the ground state. The results are thus similar to those obtained for the near ultraviolet bands of formaldehyde [see, e.g., Robinson & DiGiorgio (363)].

Innes and co-workers (191, 279, 280, 392) have carried out high resolution studies for the three isomeric diazines viz. pyridazine (1:2), pyrimidine (1:3), and pyrazine (1:4). Each of these molecules approximates very closely to a symmetric top, and furthermore the rotational constants for the molecules in their first excited singlet states are very similar to those for the ground states. Since the transition moments are perpendicular to the molecular plane for all these molecules, the bands show P , Q , R structures characteristic of parallel bands of a symmetric top. The various sub-bands coincide almost exactly, giving rise to simple rotational structures that can be resolved. The analyses confirm the assignments of the bands to $\pi \rightarrow n$ transitions (N.B. the use of $n \rightarrow \pi$ appears to have become established in the literature, although according to conventions that apply to most fields of spectroscopy the upper state should precede the lower state and the transition be written $\pi \rightarrow n$). From the vibrational analyses of the band systems, the authors conclude that pyridazine is probably planar in its excited state, while pyrimidine and pyrazine are slightly non-planar. A similar investigation of the $\pi \rightarrow n$ transition of *s*-tetrazine has been carried out by Mason (266).

VIBRONIC INTERACTIONS

Several investigations, both theoretical and experimental, have been devoted to the study of the coupling of electronic and vibrational levels in

polyatomic molecules. When the coupling is large, the levels can no longer be classified as electronic and vibrational levels, but only as vibronic levels. There are two effects of major importance, the Jahn-Teller effect and the Renner effect.

Jahn-Teller effect.—According to the theoretical arguments of Jahn & Teller (203), symmetrical configurations of non-linear molecules are unstable in orbitally degenerate electronic states. The forces that tend to destroy the symmetrical configuration of the molecule, however, are expected to be important only if the degenerate electrons participate strongly in the bonding of the molecule. Jahn (202) also showed that spin degeneracy can produce instability, but this effect is of minor importance except when the spin-orbit coupling is large. In addition to the configurational distortion predicted by the Jahn-Teller theorem, known simply as the "static Jahn-Teller effect" [see also Liehr & Ballhausen (250), Öpik & Pryce (314)], there are also dynamic effects due to the coupling of electronic and vibrational motions. This vibronic coupling, or "dynamic Jahn-Teller effect" has been discussed in papers by Longuet-Higgins *et al.* (254), Moffitt & Liehr (285), Moffitt & Thorson (286) and Van Vleck (406).

To date there is no clear-cut experimental evidence for a Jahn-Teller effect in any molecule in the gas phase except possibly in the vacuum ultraviolet absorption spectrum of benzene. The Rydberg states may be regarded as being formed from the ground state of the $C_6H_6^+$ ion, with electronic symmetry $^2E_{1g}$, together with a Rydberg electron. The molecule would therefore be expected to be distorted in conformity with the Jahn-Teller theorem. In three of the Rydberg series, Wilkinson (420) observed progressions of unusual length (up to 4 members) involving the degenerate bending vibration ν_{18}' , and concluded that the stable equilibrium configuration in each of these Rydberg states is of D_{2h} symmetry. This interpretation has been discussed theoretically by Liehr & Moffitt (251), who show, furthermore, that the selection rules for the ν_{18} mode are $\Delta v = 0, 1, 2 \dots$ rather than the $\Delta v = 0, 2, 4 \dots$ used by Wilkinson.

In the analysis of the 1600 Å band system of ammonia (see above) it was shown that the excited state is an orbitally degenerate state ($^1E''$) but no evidence was found either for configurational distortion or for irregularity in the spacing of the vibrational levels. Several authors (69, 287, 416, 417) have sought evidence for a Jahn-Teller effect in the vibrational spectra of some of the hexafluorides of the transition elements. The molecules ReF_6 , OsF_6 , and IrF_6 should have electronically degenerate ground states, while other hexafluorides, e.g., SF_6 , SeF_6 , MoF_6 , TaF_6 , WF_6 and UF_6 have non-degenerate ground states. Some anomalies in the infrared and Raman spectra of ReF_6 and OsF_6 , involving in particular the degenerate vibration ν_2 and its combination bands, have been attributed to a Jahn-Teller effect, but unfortunately similar anomalies are not found in the spectrum of IrF_6 . The evidence is therefore inconclusive.

The Jahn-Teller effect has been invoked on several occasions to account

for phenomena observed in solid state studies, but it is difficult to judge to what extent these assignments may be regarded as unambiguous. Abragam & Pryce (3) use the effect to explain the paramagnetic resonance spectrum of $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$, while Orgel & Dunitz (315) and Hepworth, Jack & Nyholm (170) attribute the asymmetry of the $\text{Mn}^{2+}(\text{F}^-)_6$ octahedra in MnF_3 to a Jahn-Teller effect. Other examples are discussed in papers by Cotton & Meyers (76), Ford & Hill (136), Knox (226), Liehr (249), Liehr & Ballhausen (250), Snyder (379), and Van Vleck (407).

Renner effect.—For a linear polyatomic molecule, orbital degeneracy does not necessitate a configurational distortion of the molecule. The coupling of the electronic angular momentum with the angular momentum associated with the bending vibrations of the molecule, however, leads to interesting dynamic effects that were first visualised by Herzberg & Teller (180) and discussed in detail by Renner (358). As an example let us consider a linear symmetrical AB_2 molecule with a lone π electron on the A atom. When the molecule bends, the π orbital may lie either in the plane of bending or perpendicular to it. Let V^+ and V^- denote the corresponding two potential curves, where V^+ denotes the upper and V^- the lower curve. Renner calculated the vibronic energy levels for a molecule in an electronic Π state and expressed the results in terms of a parameter ϵ , where

$$\epsilon = \frac{V^+ - V^-}{V^+ + V^-}.$$

He also showed that while large electronic-vibrational interactions might be expected for molecules in Π states, smaller effects are expected for Δ , $\Phi \dots$ states.

The first experimental example of the Renner effect was found in the electronic absorption spectrum of the NH_2 free radical [Dressler & Ramsay (111, 112)]. For this molecule the two combining states correlate with a $^2\Pi$ state, but whereas in the normal Renner effect both components are stable in the linear configuration, for NH_2 only the upper state has a linear equilibrium configuration and the lower state is stable in a bent configuration with an angle of ~ 103 degrees. The spectrum consists principally of a long progression $(0, v_2', 0) \leftarrow (0, 0, 0)$ of the bending vibration v_2' in the excited state, and bands with $v_2' = 1, 2, 3 \dots 20$ have been analysed. The "vibrational" levels in the excited state consist alternately of Σ , Δ, \dots and Π, Φ sub-levels, and large splittings, of the order of a few hundred cm^{-1} , are found within groups of these sub-levels. More than 100 vibronic levels for NH_2 and ND_2 have now been identified (see above). The simple theory of Renner has been extended for the NH_2 radical by Pople & Longuet-Higgins (341) and gives a satisfactory agreement with the experimental data.

A second example of the Renner effect has been found in the spectrum of the NCO free radical [Dixon (104)]. The ground state of this radical is a $^2\Pi$ state and the observed vibronic splittings agree fairly well with those predicted by Renner if (i) the spin splitting is neglected and (ii) it is assumed

that $\epsilon = -0.16$. Actually the spin splittings are comparable to the "Renner splittings" for this molecule, and a more complete theory, in which the interactions of Λ , σ , and S are taken into account, has been worked out by Pople (340).

LARGER POLYATOMIC MOLECULES

THEORETICAL

General methods for calculating π -electronic structures of polyatomic molecules have been discussed by Fukui *et al.* (143), Nishimoto & Fujishiro (308), and Zauli (432). A theoretical treatment of the difference in energies ($\sim 3800 \text{ cm}^{-1}$) for the ${}^1B_{2u} \rightarrow {}^1A_{1g}$ transitions (2600 Å systems) of benzene and hexamethylbenzene has been given by Gray, Ross & Yates (153). The calculations of Anno (12) on the singlet levels of pyridine suggest that a hidden $\pi \rightarrow n$ transition (${}^1A_2 \rightarrow {}^1A_1$) lies in the region of the strong 4.8 eV band assigned to a $\pi \rightarrow \pi$ transition. The lower triplet levels of pyrazine have also been treated by Anno & Sadô (13). The $\pi' \rightarrow n$ transitions of pyridine, pyridazine, and pyrimidine and their chloro-derivatives have been discussed by Favini & Simonetta (126, 129). Calculations have been carried out for the following five-membered ring compounds: cyclopentadiene, furan and thiophen [Mangini & Zauli (265)], thiophen and selenophen [Milazzo & De Alti (281)], and azulene and pyrazole [Brown & Heffernan (52)]. The oscillator strengths for the first four singlet transitions of naphthalene and the isoelectronic quinolinizinium cation have been calculated by Peacock (332). Other calculations on π -electronic structures include borazole [Patel & Basu (330)], acetanilide [Baba & Susuki (15)], diarylethylenes [Drefahl & Rasch (110)], *o*-quinone and diphenoquinone [Kuboyama (237, 238)], indoxazene and anthranil [Re (353)], some biphenyl derivatives of butadiene and hexatriene [Fernández-Alonso & Palou (131)], and a new class of hydrocarbons containing partially aromatic, condensed ring systems [Pauncz & Cohen (331)].

The free electron model has been used by Kuhn and co-workers to study the electronic structures of the polymethines (240), polyenes, and polyacetylenes (24, 25). Similar calculations have been carried out by Ham (165) for azulene, $C_8H_8^-$ and $C_7H_7^+$, and by Rivière (359) for conjugated dialdehyde-anions. Longuet-Higgins & Salem (255) have given a theoretical interpretation of the visible and ultraviolet spectra of the cyclic polyenes $C_{18}H_{18}$, $C_{24}H_{24}$ and $C_{30}H_{30}$ and conclude that the C—C bonds in these molecules alternate in length.

ELECTRONIC AND VIBRATIONAL ASSIGNMENTS

Some interesting work has been carried out on the 3200 Å band system of naphthalene by Craig and co-workers (79, 80). One unusual feature of this system is that the bands allowed by the electronic selection rules are very weak ($f \sim 0.0002$) and account for only 10 per cent of the total intensity of the system. The major portion of the intensity of the system is attributable to bands that derive their intensity from the next absorption system to shorter

wavelengths, by vibronic mixing of the two excited states. The electronically allowed bands are polarised parallel to the long axis (y -axis) of the molecule while the vibronically induced bands are polarised parallel to the short axis (z -axis) of the molecule [cf. McClure (271)]. Craig *et al.* (79) found that the electronically allowed bands show single heads in the vapor spectrum, whereas the vibronically induced bands all have double heads, which are separated by 2.4–3.0 cm^{-1} . The band contours thus provide a valuable criterion to aid the band assignments. The crystal spectrum of naphthalene at 4°K. has been studied by Craig *et al.* (80) while the fluorescence spectrum has been investigated by Bolotnikova (40) and Pesteil (334). The absorption spectrum of anthracene vapor has also been studied by Lyons and Morris (261).

Approximately 200 bands of benzonitrile in the region 2670 to 3010 Å have been observed in emission from a Schüler-type discharge tube by Kahane-Paillous (216). A vibrational analysis is given in terms of 16 ground state and 6 excited state frequencies. The (0, 0) band is at 36,517 cm^{-1} and the electronic transition is of the type ${}^1B_1 \rightarrow A_1$. A similar investigation of the emission spectrum of aniline has been carried out by the same author (216).

The near ultraviolet absorption spectra of *o*-, *m*- and *p*-chlorobenzaldehyde have been studied by Patel (329), and Padhye & Viladkar (320). The latter authors assign the longest wavelength absorption system for each molecule to a $\pi^* \rightarrow n$ transition and place the (0-0) bands at 25,943 cm^{-1} for the *ortho*-, 26,694 cm^{-1} for the *meta*-, and 26,807 cm^{-1} for the *para*-compound. The next absorption system to shorter wavelengths is assigned to a $\pi \rightarrow \pi^*$ transition, and the (0-0) bands are given at 33,468 cm^{-1} for the *ortho*-, 33,791 cm^{-1} for the *meta*-, and 35,097 cm^{-1} for the *para*-compound. Vibrational assignments are also discussed for the three molecules.

The absorption systems of *o*-, *m*- and *p*-chlorobenzotrifluorides in the region 2300 to 2800 Å have been studied in the gaseous, liquid and solid phases by Rao & Rao (350) and extensive vibrational assignments given. Similar vibrational analyses have been carried out for the *o*- and *m*-thiocresols [Bapat (23)] and for *p*-benzoquinone [Anno & Sadô (14)]. An investigation of the ultraviolet absorption spectra of phenylacetylene and diphenylacetylene by Padhye & Rao (318) reveals that, whereas phenyl vibrations are excited in the upper state for the former compound, acetylenic vibrations are excited for the latter compound.

The near ultraviolet absorption spectra of acraldehyde and crotonaldehyde in the vapor phase have been studied by Inuzuka (192) and the bands assigned to $\pi^* \rightarrow n$ transitions. Progressions involving the C=C and C=O stretching vibrations and one of the skeletal bending vibrations in the excited state were identified. From Franck-Condon considerations it was estimated that the C=O bond is longer in the excited state by ~ 0.1 Å. Rao & Rao (351) have also studied the long wavelength system of crotonaldehyde and give a vibrational analysis in terms of ten fundamentals in each of the lower and upper states. The (0-0) band is at 3774.1 Å. Prugger & Dörr

(345) have studied the absorption spectra of several cyclic ketones in the Schumann region and have assigned bands in the region of 51,000 to 60,000 cm^{-1} to σ^*-n transitions.

Mason (267) has continued his studies on N-heteroaromatic systems and has assigned the $\pi-\pi$ transitions for some monocyclic amino- and mercaptotazines and their ions. He has also studied the spectra of various analogues of the cinnamoyl anion and of quaternary iodides. The $\pi-n$ absorption spectra and $\pi-\pi$ phosphorescence spectra of some mono- and diazanaphthalenes have been discussed by Müller & Dörr (293). The excited states of *o*-, *m*- and *p*-dinitrobenzene have been discussed by Abe (1) together with the changes in the spectra produced by treating various nitrobenzenes with alkali (2).

Several investigations have been carried out on substances in the solid state. Hochstrasser (183) has studied single crystals containing pyrene in polarised light and has identified the first two excited singlet states as $^1B_{3u}$ states, in disagreement with theoretical predictions. Other polarisation studies have been carried out on diphenylene [Hochstrasser (183)], 1,2-benzanthracene [Brodin & Soskin (48)], tetramethyl-*p*-phenylenediamine [Albrecht (6)], diphenylmethane dyes [Adam (5)], and various polyenes and cyanines [Eckert & Kuhn (120)]. The emission and absorption spectra of perylene in the region 3800 to 5500 Å have been investigated by Shpol'skii & Personov (376) and vibrational assignments given.

EFFECTS OF SUBSTITUENTS

The effects of substituents on the frequencies and intensities of absorption bands of organic compounds continue to be the subject of many investigations. The following terms are used: bathochromic shift—towards longer wavelengths, hypsochromic shift—towards shorter wavelength, hypochromic—decreased intensity, hyperchromic—increased intensity. Attempts are made to explain the shifts in terms of various effects (e.g., mesomeric and inductive) and to relate the magnitudes of these effects to other empirical quantities, e.g., Hammett's σ factors.

Groups of compounds that have been studied include various acetylenic compounds [Romanet & Wojtkowiak (366)], aliphatic ketones [Mountcastle, Smith & Grove (291)], thiones [Janssen (205), Zahradník (430)], nitriles [Schurz, Zah & Ullrich (373)], phenylureas [Tsuzuki, Motoki & Migita (399)], phenylarsines [Cullen & Hochstrasser (84)], phenols [Shergina *et al.* (374)], catechols [Yamada (425)], fluorobenzenes and chlorobenzenes [Forbes (133, 134)], fluoroxylenes [Padhye & Varadarajan (319)], monosubstituted benzenes containing a Group VI element in the substituent [Kiss & Muth (224)], acetophenones and benzoic acids [Horton & Robertson (187)], nitroacetophenones and nitrobenzaldehydes [Lutskii & Alekseeva (260)], nitrophenethylanilines [Izmail'skii & Limanov (199)], nitrodiphenylamines [Izmail'skii & Nuridzhanyan (200)], various aromatic nitro-compounds [Conduit (74)] and their chloro-derivatives [Favini & Simonetta (127)], benzenesulfonamides and phenylsulfone derivatives [Momose, Ueda & Goya (288)], alkylpyridines [Cinsa & Fiorenzi (68)], styryl- and phenylethnyl-

pyridines [Katritzky, Boulton & Short (219)], aromatic chloroazines [Favini & Simonetta (128)], alkyl- and phenyl-substituted pyrylium salts [Balaban, Sahini & Keplinger (18)], diphenyl ethers and diphenylamines [Modena (283)], diaryliodonium salts [Irving, Turner & Reid (193), Beringer & Lillien (34)], 9-substituted acridines [Zanker & Reichel (431)] and various derivatives of tetraphenylmethane [Levrushin (246)], 1:3:5 triazine [Hirt, Halverson & King (181)], 1,2,4 oxadiazole [Barrans (27)], thiazole [Okamiya (311), Al'perovich, Grechko & Ushenko (10)], pyran-2, 4-dione [Chandross & Yates (64)], azulene [Treibs & Borsdorf (393), Anderson & Steckler (11)], anthracene [Cherkasov (65)], anthracene, phenanthrene, and 3:4 benzophenanthrene [Jones & Spinner (210)], phenylisoquinoline [Berti & Corti (35)], and *p*-terphenyl [Brocklehurst *et al.* (47)].

STERIC HINDRANCE

Several authors have discussed the effects of steric hindrance on the electronic spectra of conjugated systems. Suzuki (386), in particular, has produced 11 papers on substituted biphenyls, stilbenes, styrenes, and similar compounds. For the stilbenes he notes that as the two phenyl groups are rotated in opposite directions, out of the plane of the central double bond, the "conjugation band" shifts to shorter wavelengths. The degree of rotation may be quite different for the same compound in the vapor, liquid, and solid phases. Thus, for biphenyl, Suzuki estimates that the angle between the planes of the benzene rings is 40 to 43 degrees in the vapor, 20 degrees in solution, and different again in a KBr disc. Other studies include investigations of substituted biphenyls [Moriconi *et al.* (290)], substituted stilbenes [Jaffé & Orchin (201), Bruylants, Leroy & van Meerssche (53)], *o*-chloro-substituted styrenes and benzenecarboxylic acids [Ballester *et al.* (21)], chlorinated derivatives of alkylbenzenes [Ballester & Castañer (20)], methyl-substituted benzoic acids [Pérez Ossorio (333)], benzylideneaniline [Ebara (117)], di- and tri-arylmethanes [Barker, Hallas & Stamp (26)], and benzidine diazo dyes and their copper derivatives [Kobayashi, Tanizaki & Ando (229)]. The rotational isomerism in the *N*-benzylanilines, caused by intramolecular interaction between the NH group and the π -electrons, is discussed by Oki & Mutai (312).

FLUORESCENCE AND PHOSPHORESCENCE

Many papers have appeared on the emission spectra of polyatomic molecules. The phosphorescence of benzene (and C_6D_6) in solid methane, argon, krypton, and xenon at 4.2°K. has been studied by Wright, Frosch & Robinson (424), and the spectra and lifetime of the phosphorescence were found to vary considerably from one matrix to another. Preliminary measurements of polarised phosphorescence in benzene in a rigid glass at -195°C. have been reported by Albrecht (9). Despite these new results, there is still no unambiguous experimental evidence to decide whether the lowest triplet state of benzene is a $^3B_{1u}$ or a $^3B_{2u}$ state, although theory strongly favors the former [see Craig (78)].

Stevens & Hutton (381) have studied the fluorescence intensity of anthracene vapor as a function of the exciting wavelength for the range 2300 to 3660 Å. A delayed fluorescence in phenanthrene vapor has been shown by Stevens, Hutton & Porter (382) to be attributable to anthracene impurity; the mechanism of excitation is discussed. The fluorescence yields of several solutes in a series of solvents have been measured by Bowen & Miskin (42) and were found to increase with increasing viscosity of the solution. Forster *et al.* (138) however found that a 750-fold variation in solvent viscosity is without appreciable effect on the radiative and non-radiative electronic transitions in biacetyl solutions. Hochstrasser (182, 184) has measured the relative fluorescence and phosphorescence yields of a number of molecules as a function of the wavelength of the exciting light and has obtained information concerning the internal conversion of energy in these molecules. The transfer of triplet state energy from one molecule to another, known as sensitised phosphorescence, has been studied in solution by Bäckström & Sandros (16) and found to be a diffusion controlled process. The measurements of Weber (414) on the fluorescence spectra of tyrosine, tryptophan, and related compounds show that these molecules can transfer their excitation energy to another molecule over distances ~ 20 Å. Energy transfer in molecular complexes, e.g., anthracene—1:3:5 trinitrobenzene, has been studied by McGlynn, Boggus & Elder (274).

Studies of the triplet-singlet emission spectrum of *o*-xylene at 4.2°K. by Blackwell, Kanda & Sponer (39) reveal two sharp spectra separated by 370 cm^{-1} from each other. These spectra are attributed to two distinct crystalline phases. In a similar manner, investigations of the luminescence of C_6H_6 , $\text{C}_6\text{H}_5\text{D}$, *p*- $\text{C}_6\text{H}_4\text{D}_2$, and C_6D_6 in cyclohexane at liquid nitrogen temperature by Coupron *et al.* (77) suggest two different sites of crystallisation in cyclohexane. The fine structure in the luminescence spectra of aromatic hydrocarbons at low temperatures has been attributed to microcrystallinity by Shpol'skii & Klimova (375).

Other emission studies include the luminescence of *o*-disubstituted aromatic hydrocarbons [Naboikin, Pavlova & Zadorozhnyi (299)] and substituted polyenes [Nikitin *et al.* (307)], the fluorescence spectra of biphenyls and their oxygen- and sulfur-containing analogues [Levshin *et al.* (247)], fluorescence of γ -hydroxyquinolines [Popovych & Rogers (342)] and mono- and di-aminoacridines [Wittwer & Zanker (423)], luminescence spectra of naphthols and naphthalenediols [Hercules & Rogers (171)], the $\pi^*-\pi$ phosphorescence of chlorophylls *a* and *b* [Singh & Becker (377)], and the fluorescence spectra and quantum yields for some substituted anthracenes [Cherkasov (66)].

MOLECULAR COMPLEXES

An interesting theoretical paper by Murrell (297) discusses the relation between the stability of a molecular complex and the intensity of its charge-transfer bands. Foster (139) has measured the intermolecular charge-transfer spectra of complexes formed from various *p*- π aromatic electron donor mole-

cules with a series of p - π aromatic electron acceptor molecules. The frequencies of the bands of these complexes may be expressed simply as the sum of two terms, characteristic of the donor and acceptor molecules, provided the electron donor is not too weak. Nagakura (301) has carried out studies on intramolecular charge-transfer spectra and has assigned the 1717 Å band of formamide and the 1935 Å band of acetaldehyde to such transitions. In collaboration with Hosoya & Tanaka (188), he has carried out detailed investigations of the absorption spectra of thioacetamide and thiourea, including polarised studies on single crystals, and has assigned bands to intramolecular charge-transfer bands.

Iodine complexes continue to receive considerable attention. Walkley, Glew & Hildebrand (411) note that the visible absorption peak of dissolved iodine shifts to shorter wavelengths with decreasing ionisation potential of the solvent. The solvents investigated fall into two distinct groups, known as π donors and n donors, and within each group a linear variation of shift with ionisation potential is observed. Charge-transfer complexes between iodine atoms and aromatic hydrocarbons have been observed in flash photolysis experiments by Strong, Rand & Britt (384). Spectroscopic studies of complexes involving molecular iodine include complexes of iodine with itself [De Maine, De Maine & McAlonie (94)], with KBr and KI [Daniele (90)], tributyl phosphate [Tsubomura & Kliegman (395)], diethyl ether [de Maine (95)], nitromethane [de Maine & Ahlers (96)], *NN*-dimethylaniline [Tsubomura (394)], *cis*- and *trans*-stilbene [Yamashita (426)], and naphthalene [De Maine & Peone (97)].

Hausser & Mulliken (166) have shown that a weak band at 27,500 cm^{-1} in the absorption spectrum of chloranil is due to the parent molecule and not to a charge-transfer band involving the solvent as had previously been assumed. The quenching of triplet states of anthracene and porphyrins by heavy-metal ions has been attributed by Linschitz & Pekkari (252) to a charge-transfer process. Other spectroscopic studies of molecular complexes include complexes between nitromethane and itself [De Maine *et al.* (98)], chloranil and aromatics [Kuboyama (239)], phthalocyanine and iron trichloride [Glikman & Barvinskaya (148)], benzacridine and dibenzacridine derivatives [Izmail'skii & Kitrosski (198)], and various dyes [Kobayashi, Tanizaki & Ando (228)]. Yamatera (427) has discussed charge-transfer spectra in metal complexes, while six papers on molecular complexes have been contributed by Czekalla and co-workers (44, 45; 85 to 88).

SOLVENT EFFECTS

Several authors have investigated the effects of solvents on the frequencies of absorption bands, but little, if any, work has been directed towards the associated changes in band intensities. Bovey & Yanari (41) have plotted frequency shifts against

$$\frac{n^2 - 1}{n^2 + 2}$$

for various solvents and obtained approximately linear relations, while similar results have been obtained by Sverdlova (387) using

$$\frac{n^2 - 1}{2n^2 + 1}$$

along the abscissa axis. Zhmyrev *et al.* (433) have used a more complicated function viz.

$$\frac{2\epsilon - 1}{2\epsilon + 2} + \rho \frac{2n^2 - 1}{2n^2 + 2}$$

and have tested this function for 37 different solvents. Ito, Inuzuka & Imanishi (195, 196) use a different approach in their studies on ketone bands in various solvents. They plot the shift of the infrared carbonyl band against the shift of the π - n absorption band in the ultraviolet and find an approximately linear relation. Another approach is adopted by Schubert, Steadly & Craven (372) who find approximately linear relations when solvent shifts for substituted compounds are plotted against solvent shifts for unsubstituted compounds. They attempt to relate the slopes of these graphs to the Hammett σ -constants for the substituent groups.

The effects of high pressure and low temperature on the absorption spectra of some condensed-ring aromatic compounds have been studied by Robertson (360). The electronic shifts for 11 ultraviolet transitions of polynuclear aromatic hydrocarbons in a series of 17 paraffin hydrocarbons have been discussed by Weigang (415) in terms of a statistical theory. Studies of solvent effects have been reported for the π^* - n transitions in pyrazine [Krishna & Goodman (236)], the π^* - n transitions of aliphatic carbonyl and nitro-compounds [Rao and co-workers (19, 349)], and for the fluorescence spectra of substituted naphthalimides [Yasuda *et al.* (428)].

HYDROGEN BONDING

Investigations of the effects of hydrogen bonding on the ultraviolet absorption spectra of various compounds, e.g., phenols and benzoic acids, have been carried out by Ito and co-workers (194, 197). The effects of change of concentration and change of temperature on the ultraviolet absorption spectra have been studied, and the results were sometimes correlated with those derived from infrared studies. It was found that all the absorption spectra characterised by π^* - π transitions exhibit a large red shift and an increase in total absorption intensity when hydrogen bonds are formed between the solute and solvent molecules. For some π^* - n transitions, however, it was found that hydrogen bonding was accompanied by a blue shift and a decrease in the total intensity of the bands.

Julg & Bonnet (215) have carried out spectroscopic investigations of hydrogen bonding between amines and phenols, while Dearden & Forbes (91) have obtained evidence for both inter- and intramolecular hydrogen bonding in various anilines and phenols. Studies of the absorption spectra of

some nitroanilines [Lutskii & Alekseeva (259)] and of the luminescence spectra of some *o*-disubstituted aromatic carboxylic acids [Naboikin, Zadorozhnyi & Pavlova (300)] suggest that these compounds also exhibit intramolecular hydrogen bonding.

OTHER WORK

Evans (123) has continued his interesting work on the effect of paramagnetic substances on forbidden transitions. He finds that the triplet-singlet absorption bands of ethylene, butadiene, hexatriene, and a number of other conjugated olefins can be induced by oxygen at high pressures. Similar effects are also found for diacetylene and a number of substituted diacetylenes. The theory of this phenomenon has been discussed by Hoijsink (185), Murrell (298), and Tsubomura & Mulliken (396). The last authors also present some additional experimental results.

The subject of exciton splitting of bands in crystals, known as Davydov splitting, continues to receive attention. A summary of data on the benzene homologues is given by Broude & Onoprienko (51) who also discuss the shapes and widths of absorption bands and the sensitivity of the spectrum of a crystal to small changes in structure. New data on C_6H_6 , C_6D_6 , and mixed crystals of the two, have been reported by Ciaisi & Pestil (67), who have also studied naphthalene in octodeuteronaphthalene (335). The theory of the crystal splittings for phthalocyanine has been given by Lyons, Walsh & White (263), while predictions of the crystal spectrum of coronene have been made by Lyons & Walsh (262).

A few papers have appeared on the spectra of adsorbed molecules. Kobayashi (227) has investigated the absorption spectra of phenol and *p*-toluidine adsorbed on various solid surfaces, while similar studies have been made by Kotov & Terenin (231) for aromatic amines adsorbed on aluminosilicate catalysts. Absorption and reflection measurements have been carried out for anthracene adsorbed on alumina [Voyatzakis *et al.* (410)] and for a dye adsorbed on a crystal [Boyer (43)].

INORGANIC MOLECULES

LIGAND FIELD STUDIES

The spectrum of an atom or an ion with an incomplete *d*- or *f*-shell may be greatly modified by the electric field due to surrounding atoms, ions, or molecules, which are known generally as ligands. Ligand field theory attempts to explain how the frequencies and intensities of the transitions vary with the strength and symmetry of this electric field. The results are usually discussed in terms of a diagram in which the energy levels are plotted against a parameter that measures the electric field strength. Earlier work in this field has been admirably summarised in reviews by Griffith & Orgel (155), McClure (272) and Moffitt & Ballhausen (284).

In the present year Gilde & Bán (147) have calculated the terms arising

from d^n -configurations ($n=1, \dots, 10$) in strong fields of tetragonal (D_{4h}) symmetry. Griffith (154) has given a theoretical discussion of spin-orbit coupling energies in octahedral complexes, while McLellan (278) has derived selection rules for spin-orbit matrix elements for the configuration f^n . Jørgensen (212) has discussed complexes of the transition groups involving d and f electrons. On the experimental side, numerous papers have appeared and will be classified, where possible, in terms of the element involved, the outer electron configuration, and the symmetry of the surrounding electric field. These studies are as follows: Cr^{3+} ($3d^3$) in glasses, octahedral symmetry [Bates & Douglas (31)]; Cr^{3+} ($3d^3$) in fields with D_{3d} , C_3 , C_{2h} , and C_i symmetries [Schmitz-du Mont & Reinen (371)]; Mn^{2+} ($3d^5$) in MnCl_2 and MnBr_2 , cubic symmetry [Pappalardo (327), Stout (383)], also hydrated manganese salts [Tsujioka & Couture (398)]; Fe^{2+} ($3d^6$) and Co^{3+} ($3d^6$) in fields with O_h , T_d , D_{4h} , D_{3d} , and D_{2h} symmetries [Cotton & Meyers (76), Low & Weger (258)]; Co^{2+} ($3d^7$) in coordination compounds with tetrahedral and octahedral symmetries [Ferguson (130), Furlani & Geroni (144)]; Ni^{2+} ($3d^8$) in molten NiCl_2 with nearly tetrahedral coordination [Sundheim & Harrington (385)]; Cu^{2+} ($3d^9$) in tetragonal fields [Graddon (152), Ross & Yates (367), Royer (368)]; Ce^{3+} ($4f$), Pr^{3+} ($4f^2$) and Nd^{3+} ($4f^3$) in cubic fields [Mandel, Bauman & Banks (264)]; Pr^{3+} ($4f^3$) in fields with D_{3h} symmetry [Hellwege, Hess & Kahle (168)]; Sm^{3+} ($4f^6$), trigonal (C_{3v}) symmetry [Friedrich, Hellwege & Lämmermann (141)]; Eu^{3+} ($4f^6$), D_{3h} or C_{3h} symmetry [Judd (214)]; Dy^{3+} ($4f^9$), C_{3v} symmetry [Ford & Williams (137)]; Er^{3+} ($4f^{11}$), D_{3h} , C_{3h} , and C_2 symmetries [Hellwege, Hüfner & Kahle (169)]; Tm^{3+} ($4f^{12}$), C_{3h} symmetry [Gruber & Conway (162)]; Yb^{3+} ($4f^{14}$), cubic symmetry [Low (257)]; and Re^{4+} ($5d^3$), cubic symmetry [Eisenstein (121)]. Other studies have been carried out on the following ions: Cr^{3+} ($3d^3$) [Tsujioka (397), Ford & Hill (135, 136)]; Mn^{2+} ($3d^5$) [Tsujioka (397)]; Fe^{3+} ($3d^5$) [Rao & Rao (352)]; Ni^{2+} ($3d^8$) [Lehotai (245), Nortia (309)]; Dy^{3+} ($4f^9$), Ho^{3+} ($4f^{10}$) and Tm^{3+} ($4f^{12}$) [Crosby & Whan (81, 82)]; Er^{3+} ($4f^{11}$) [Van Uitert & Soden (405)]; and U^{4+} ($5f^2$) [Conway (75), Galkin & Feofilov (145)].

MATRIX STUDIES

Further studies have been carried out on the emission and absorption spectra of small molecules trapped in matrices at low temperatures. Earlier work in this field has been summarised by Franklin & Broida (140), and Ramsay (347). The absorption spectra of solid methane, ammonia, and ice have been investigated by Dressler & Schnepf (113) and that of α -oxygen by Hörl (186). Some of the assignments of band systems observed in emission when the products of discharges through nitrogen and oxygen are condensed at liquid helium temperature have now been checked by Broida & Peyron (50) using isotopic substitution. In particular, they assign their A -bands to the Herzberg system of oxygen ($A \ ^3\Sigma_u^+ - X \ ^3\Sigma_g^-$) and another system (M -bands) to the $^4\Pi - X \ ^2\Pi$ intercombination system of NO. Nicholls & Krishnamachari (305) have observed an emission spectrum between 3000 and 4600

A when the products of discharges through N_2 and CO are condensed at 4°K. The bands are assigned to NCO, but from the intensity distribution in the observed spectrum it would appear to the reviewer that most of the vibrational assignments given by these authors are incorrect.

Robinson and McCarty have continued their studies of small transient species trapped in inert gas matrices at 4.2°K. and have reported absorption spectra of NH, PH, OH, CH, CN, C_2 , NH_2 , PH_2 , HCO, HNO, and NCO (268, 269). They have also attempted to explain the shifts between the absorption bands of species in the gas and solid phases, in terms of a Lennard-Jones potential between the trapped species and the rare gas atoms (270). The photolysis of diazomethane in matrices at low temperatures has been studied both by Robinson & McCarty (364) and by Goldfarb & Pimentel (149), and some new bands were found in the region of 2600 to 4000 Å. These bands have been tentatively assigned to CH_2 or possibly CN_2 or HCN_2 . In addition, Goldfarb & Pimentel (150) have observed an orange-red luminescence when the products of photolysis are allowed to warm up, and tentatively assign the emission to a $Z \rightarrow V$ transition of ethylene.

OTHER WORK

Several investigations of the absorption spectra of semiconducting crystals at low temperatures have been carried out, notably by Gross and his collaborators (157 to 160) [also Reiss & Nikitine (357)]. A useful summary of this work is given in the introduction to (160). The long wavelength edge of the absorption region frequently shows discrete structure, which some authors relate to the formation of exciton states in crystals while others attribute it to the presence of impurities of the crystal lattice.

The absorption spectra of thin films of all the alkali halides have been studied by Eby, Teegarden & Dutton (119), and similar measurements have been carried out on the thallous halides [Tutihasi (400)] and uranium dioxide [Ackermann, Thorn & Winslow (4)]. Fischer (132) has investigated the exciton spectra of the alkali halides, while the shape of the F -band absorption in potassium chloride has been discussed by Konitzer & Markham (230). The α - and β -bands of NaF, NaCl, and KCl, which appear when the alkali halides are bombarded with x-rays, have been studied by Onaka & Fujita (313).

The ultraviolet absorption spectrum of the iodide ion has been studied by Jortner, Raz & Stein (213), and the effects of environmental changes have been investigated by Griffiths & Symons (156). Carrington, Symons, and co-workers (17, 59, 60) have continued their studies of the oxyanions of the transition metals, while several workers have been interested in the absorption and fluorescence spectra of uranyl salts [Pant *et al.* (323, 324, 325), Bist (38), Pande (321), Narasimham & Rao (303), Sinyakova & Klassova (378)]. The visible bands of many aquo-ions, e.g., $Ni(H_2O)_6^{++}$ and $Co(H_2O)_6^{++}$, were found by Halpern & Harkness (164) to shift to higher frequencies when D_2O replaces H_2O . Some conclusions by Golding (151) concerning the absorption spectra of aqueous solutions in the region 1850 to 2000 Å have been rejected

by Barrett & Mansell (28) and by Price *et al.* (344), who have studied the spectra of liquid H_2O , HDO , and D_2O in this region.

Several other investigations of the spectra of organometallic compounds and chelates have been reported but space does not permit inclusion of this work.

SUMMARY

Steady, though not spectacular, progress has been made on several fronts. With the number of high resolution grating spectrographs increasing, considerable advances can be expected in our knowledge of the electronic structures of simple molecules. Of particular interest among recent developments are the investigations of the CH_2 and CH_3 radicals, the elucidation of the naphthalene spectrum, the studies of vibronic interactions in simple polyatomic molecules, and the investigations of the influence of paramagnetic substances on singlet-triplet transitions.

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VIBRATION-ROTATION SPECTROSCOPY¹

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The authors of this contribution to the series on molecular spectroscopy have gratefully exercised the prerogative of selecting a limited number of topics for discussion rather than attempting an all inclusive coverage of the literature. We shall, therefore, emphasize work of a general nature on fine structure and perturbation effects, internal rotation, computational methods, double minimum potential functions, and condensed phase spectra. Readers interested in recent spectra of specific molecules are referred to the *Chemical Abstracts*. Absorption spectra from 1945 to 1957 are given in a recently published index (1).

HIGH RESOLUTION STUDIES ON SIMPLE MOLECULES

The continued interest in "simple" molecules is motivated by a desire to make quantitative investigations of previously neglected higher order perturbation effects. The availability of modern experimental techniques, by which several rotational lines may be resolved within a range of one reciprocal centimeter, has given impetus to the extension of theoretical treatments of vibration-rotation fine structure.

Benedict, Plyler & Tidwell have continued their comprehensive reinvestigation of NH_3 (2) by measuring 1800 lines in the region 2060 to 3580 cm^{-1} . [In previous work they had remeasured, at high resolution, the NH_3 absorption in the regions 2370 to 3080 cm^{-1} (3) and 4100 to 4600 cm^{-1} (4); and had discussed the magnitudes of the molecular parameters (5) for both NH_3 and ND_3 .] Lines belonging to the ν_1 , ν_3 , and $2\nu_4$ excited vibrational states of NH_3 were identified. The analysis of the rotational structure of the ν_3 band was accomplished without resort to exotic interactions. On the other hand, the ν_1 fundamental shows a Fermi resonance with the parallel component of $2\nu_4$ and a Coriolis resonance with the perpendicular component of $2\nu_4$. The $2\nu_4$ band indicates a strong Coriolis interaction between the $\ell=0$ and the $\ell=2$ states. The analysis also yields extensive new information regarding the dependence of the inversion splittings on vibrational and rotational quantum numbers. Although identifications and assignments were accomplished in this study, it was not possible to derive molecular parameters that could reproduce the spectra, presumably because of the need for a more detailed theory. [See (6) and the discussion below.]

Garing, Nielsen & Rao (7) have similarly remeasured the NH_3 absorption at lower frequencies, 1440 to 1840 cm^{-1} and 510 to 1280 cm^{-1} . Their analyses involved the ν_4 , ν_2 , and $2\nu_2$ excited vibrational states. Here again a complete

¹ The survey of literature pertaining to this review was concluded in December 1960.

analysis was not possible for lack of an adequate theoretical basis of interpretation. Their assignments do, however, include numerous examples of "giant" ℓ -type doubling of the $K = \ell = \pm 1$ levels. This doubling is two to three orders of magnitude larger than the ℓ -type doubling observed in linear molecules and is effectively the sum of the degenerate ℓ -type doubling and the Coriolis interaction between the ν_4 and ν_2 vibrations. They also observe an intensity anomaly in the $2\nu_2^* \leftarrow 0^0$ overtone band, the R branch being of high intensity relative to the P and Q branches. It is suggested that this may be the result of a Coriolis interaction between $2\nu_2^*$ and ν_4 , which are only 29 cm^{-1} apart, but the theory requires further development. Their data also adds much new information about the inversion splitting dependence on vibrational and rotational quantum numbers.

In related work, Nielsen, Rao and co-workers measured the ν_4 vibrations of ND_3 (8) and the ν_2 and ν_4 vibrations of PH_3 (9); these also show the presence of "giant" ℓ -type doubling and a splitting of certain energy levels in ν_2 and ν_4 excited states of PH_3 .

In an attempt to elucidate some of the results discussed in the above paragraphs, Weeks, Hecht & Dennison (6) have extended the theory of the ammonia inversion to include inversion-vibration and inversion-rotation interactions. To approximate the potential energy of ammonia they used the potential of a system of harmonic oscillators in five vibrational coordinates, plus a double minimum function $V(\xi)$, which was chosen to have the form

$$V(\xi) = 2F \cos(\xi/L) + 2G \cos(2\xi/L) \quad 1.$$

with ξ the inversion coordinate and L a constant. Inversion-vibration interactions were obtained through a Taylor series expansion of the parameters F and G in the five vibrational coordinates. The success of this function is only partial since, although the dependence of the inversion-vibration splitting on the vibrational quantum numbers of the two doubly degenerate modes is accounted for (with the exception of the state $2\nu_4^0$), the interaction between the inversion coordinate and the remaining mode is not correctly predicted. The calculated and observed inversion splittings are compared in Table I.

TABLE I
COMPARISON OF CALCULATED AND OBSERVED INVERSION SPLITTINGS

Level $n_1 n_2 n_3 n_4^t$	Calc.	Obs. cm^{-1}	Level	Calc.	Obs. cm^{-1}
001 ⁰ ₀	(.34)	.35	011 ⁰ ₀	19.39	18.49
002 ⁰ ₀	.46	.43	010 ⁰ ₁	43.10	45.4
000 ⁰ ₁	(1.04)	1.04	011 ¹ ₁	23.00	23.68
000 ⁰ ₂	1.33	1.42	110 ⁰ ₀	(25.32)	25.55
000 ⁰ ₂	1.34	2.24	100 ⁰ ₀	.51	.99
001 ¹ ₁	.42	.57	100 ¹ ₁	.58	.86

Inversion-rotation constants calculated from the lowest order Hamiltonian compare well with observation, but it was suggested that some of this agreement is fortuitous.

Plyler, Tidwell & Blaine (10) have re-examined the absorption by CH_4 in the ν_3 fundamental region at high resolution and low pressures. They report 2460 lines in the region 2450 to 3200 cm^{-1} . The interpretation suggests the appearance of lines, in addition to those of the standard ν_3 spectrum, caused by isotopic variants, hot bands, components of $2\nu_2$, $\nu_2 + \nu_4$, and $2\nu_4$, and of "forbidden" lines of ν_3 activated by interactions. Splitting of the P , Q , R components of ν_3 is observed and qualitatively explained on the basis of Jahn's (11) theoretical treatment.

Hecht (12) has accomplished a treatment of the theory of vibration-rotation energies of tetrahedral XY_4 molecules in which it is shown that, to the third order, the splitting of a level into its tetrahedral sub-levels is governed by perturbation terms of one basic symmetry in all states in which ν_1 , ν_3 , and ν_4 are excited and, to a certain approximation, in many states in which ν_2 is excited along with ν_3 or ν_4 . The perturbation is identified as the tetrahedrally symmetric linear combination of fourth rank spherical tensor operators. In dominant approximation, the rotational fine structure splitting patterns are characterized (solely) by the rotational angular momentum of the state, with a scale factor dependent upon vibration, total angular momentum, and the vibrational character of the state. A higher approximation introduces deformation of the basic pattern caused by elements off-diagonal in the rotational angular momentum quantum number. This deformation is not negligible in terms of modern experimental capabilities of observation. In the dominant approximation, the four rotational sublevels (A_1 , F_1 , E , F_2 or A_2 , F_2 , E , F_1) are split from their center of gravity in the ratios 14, 7, 2, -13 respectively. (Note the weight factors are A , E , $F=1, 2, 3$.) Table II shows the excellent agreement of this theory with the observed splitting of lines from several bands. Hecht (13) has also successfully applied his theory to the quantitative explanation of the forbidden P and R branch lines of ν_3 as measured by Plyler *et al.* (10, 14).

Other work on methane has been subjected to analysis that employed lower order theoretical results than those of Hecht to derive basic molecular parameters. Thomas & Welsh (15) have analyzed a wealth of rotational Raman structure on the ν_2 and ν_3 fundamental bands to attain an r_0 value of 1.09403 ± 0.00016 Å. Allen & Plyler (16) have made quite detailed analyses of CH_3D bands at 2200 cm^{-1} (parallel type, ν_2) and at 2780 cm^{-1} (perpendicular type, $\nu_3 + \nu_3$), and of the CD_3H band at 2600 cm^{-1} (hybrid type, $2\nu_3$). Rank, Eastman, Skorinko & Wiggins (17) have examined the fine structure splitting of P , Q , R branch lines of the $2\nu_3$ band of CH_4 using a Fabry Perot etalon with resolving power of 400,000.

In other high resolution studies Rank and co-workers (18) observed and analyzed several cases of Fermi resonance in the 1 to 3 μ region of the HCN spectrum. Several combination bands of CH_3CN were analyzed by Dick &

TABLE II
OBSERVED FINE STRUCTURE PATTERNS FOR STATES WITH A
ROTATIONAL ANGULAR MOMENTUM, $R=4$

Theory (Dominant approximation)	$\nu_3 P(4)^*$	$\nu_3 Q(4)^*$
$A_1(A_2)+14$	$A_1+14.0 \times (0.0138 \text{ cm.}^{-1})$	$A_2+14.0 \times (-0.0173 \text{ cm.}^{-1})$
$F_1(F_2)+7$	$F_1+7.0$	$F_2+7.5$
$E+2$	$E+2.3$	$E+4.4$
$F_2(F_1)-13$	$F_2-13.3$	$F_1-15.0$
$\nu_1+\nu_4 P(4)^\dagger$	$\nu_4 P(4)^\ddagger$	$\nu_2+\nu_3 R(4)^\dagger$
$A_1+14.0 \times (0.061 \text{ cm.}^{-1})$	$A_1+14.0 \times (0.060 \text{ cm.}^{-1})$	$A_1+14.0 \times (0.022 \text{ cm.}^{-1})$
$F_1+7.1$	$E_1+7.7$	$F_1+8.0$
$E+1.8$	$F+2.5$	$E+3.8$
$F_2-13.0$	$F_2-14.0$	$F_2-15.2$

* See Ref. (10).

† See Ref. (135).

‡ See Ref. (136).

Meister (19) to give rotational constants and zeta values ($\zeta_5=0.071$ and $\zeta_6=-0.407$) that agree nicely with those of Parker, Nielsen & Fletcher (20) ($\zeta_5=0.073$ and $\zeta_6=-0.390$). In the series investigating forbidden transitions in diatomic molecules, Durie & Herzberg (21) have analyzed the rotation-vibration spectrum of HD. The background and theory of high resolution Raman spectroscopy has recently been comprehensively reviewed by Stoiceff (22), and he and his colleagues have also continued their extensive researches in this field (23, 24). The Raman spectrum of allene, studied by Brodersen & Richardson (25) with 0.4 cm.^{-1} resolution, shows a rotational perturbation in the Q branch occurring at higher values in the Raman than were found in the infrared (26). Extensive information on Coriolis effects in several bands of allene is given by the infrared work of Eaton & Thompson (27).

With the many high-resolution grating spectrometers now in use, a need has occurred for very accurate wavelengths to be used in calibration. Plyler, Danti, Blaine & Tidwell (28) have tabulated, and remeasured where necessary, suitable bands of readily available common gases for this purpose, accurate to about 0.03 cm.^{-1} throughout the region 2 to 16μ and providing good calibration points at frequent intervals. Although HCl and HBr are tabulated among the above gases, two separate papers (29, 30) report these spectra to 0.01 cm.^{-1} not only for use in precise calibrations but also to present the highly accurate rotational constants yielded by these data. They note also that the recently reported pressure shifts (31) need not be considered for

most work where measurements to 0.01 cm^{-1} are satisfactory for calibration. Also for use as standards, Rank, Skorinko, Eastman & Wiggins (32) have critically analyzed the recent infrared measurements from their laboratory to obtain highly precise wavelengths of selected bands of HCN and CO.

PRESSURE EFFECTS ON SPECTRA

Another field opened to experimental study through the availability of high resolution infrared spectrometers is the study of individual line shapes and shifts attributable to intermolecular interactions at low pressures. Kimel, Hirshfeld & Jaffé (31) reported studies on the $2 \leftarrow 0$ HCl³⁵ and HCl³⁷ bands showing line shifts of $\pm 0.015 \text{ cm}^{-1}$ over pressure ranges below 1 atm. Lines near the band center were blue-shifted, but both *P* and *R* branch shifts, strongly *J* dependent, became red-shifted at high *J* values with the larger shifts occurring in the *R*-branch. Their results were confirmed quantitatively by Rank, Birtley, Eastman & Wiggins (33) and the investigators of both groups extended the study to include broadening and shifting of the $2 \leftarrow 0$ HCl lines by foreign gases (33, 34). Rank *et al.* (35) have shown that the shift caused by foreign gases correlates with the optical polarizability and with the shifts observed by Anderson, Pipkin & Baird (36) on the 21-cm. line of atomic hydrogen. Rank, Eastman, Birtley & Wiggins (37, 38) extended their work to include a detailed study of line shapes in the $\nu_1 + \nu_2$ band of C_2H_2 as well as in the $2 \leftarrow 0$ band of HCl. No asymmetry of the lines perturbed by foreign gases was observed. They have also demonstrated that perturbation of the $2 \leftarrow 0$ band lines of HCl by xenon produces broadened line profiles indistinguishable from a Lorentz (collision broadened) shape. It would appear at this time, however, that no satisfactory theory for the shift of the line maxima has been advanced.

Vu & Vodar (39) examined the band envelope of the HCl fundamental as a function of both temperature and the pressure of added N_2 or A up to several hundred atmospheres, observing the development of an induced *Q* branch as foreign gas pressure is increased, especially at low temperatures. Oksengorn, Schuller & Vodar (40) have studied the effect of A, Kr, and Xe, on the HF and HCl fundamentals and found a linear relation between the density of the foreign gas and the frequency of the induced *Q* branch. Turrell, Vu & Vodar (41) have attempted a theoretical interpretation of these and other data (42, 43) following the method outlined by van Kranendonk (44, 45) in his analysis of perturbation-induced spectra in H_2 by N_2 and the rare gases. Paralleling that treatment, heterogeneous binary collisions are assumed to lead to the breakdown of the usual $\Delta J = \pm 1$ selection rule, as evidenced by the proportionality of the *Q* branch intensity to the density of each component of the mixture. In the halogen acid case, the perturbation giving rise to the induced *Q* branch seems attributable to angularly independent terms in the overlap moment, the quadrupole induction effect being relatively negligible.

One should also note the very high pressure work begun by Weir, Lippin-

cott, Valkenburg & Bunting (46). Using a recently developed high pressure cell with a pair of type II diamond windows, transparent (except at 5μ) in the region 1 to 15μ , they studied solids up to 30,000 atm. They found a pressure shift of the bands to higher frequency along with decreased intensity, and the magnitude of both changes was dependent on the mode of vibration.

INTERNAL ROTATION

The growing interest in the phenomenon of internal rotation has been underscored during the past year by the appearance of three separate review articles on this topic. Sheppard (47) has covered rotational isomerism about C—C bonds, Lin & Swalen (48) have given a general review of internal rotation and microwave spectroscopy, and Wilson's review (49) summarizes broadly the problems attendant upon measuring and predicting the magnitudes of barriers to internal rotation.

Recently a number of fresh starts have been made on the problem of predicting barrier heights. Harris & Harris (50) claim that barriers to internal rotation in ethane molecules can be accounted for by a non-ionic valence bond treatment that uses ordinary sp^3 hybrid orbitals at the carbon atoms but abandons the perfect pairing approximation. Since interactions between hydrogen atoms on different carbons were ignored in this calculation, the entire barrier height is attributable to deviations from perfect pairing. However, Karplus (51), using an identical treatment except for somewhat different approximations in evaluating the molecular integrals, comes to the contrasting conclusion that such deviations from perfect pairing make only an insignificant contribution to observed barrier heights. Karplus has indicated one way in which the reliability of the two calculations might be tested. The calculation of barrier heights and theoretical nuclear spin coupling constants of protons on adjacent carbon atoms involve essentially the same computations (52). Thus the dependence of the proton-proton coupling constants on the angle of internal rotation must be correctly reproduced by a reliable calculation of the barrier to internal rotation. At present, the limited experimental data (53, 54) appears to be in agreement with the spin coupling constants calculated by Karplus. It is unfortunate, for the sake of this test, that Harris and Harris did not report their ground state electronic wave functions. If deviations from perfect pairing are ignorable, then d and f orbitals on the adjacent carbon atoms of ethane molecules can be invoked to explain barriers to internal rotation. This idea, suggested a long time ago by Eyring (55), has been recently revived by Pauling (56). For a critical analysis of the Eyring-Pauling theory the reader is referred to Wilson's review article on barriers to internal rotation (49).

An entirely different approach to the internal rotation problem, making use of the virial theorem, has been proposed by Clinton (57) and is really in the form of a question. By virtue of the virial theorem, the energy difference ΔW between the staggered and eclipsed configurations of ethane is

$$\Delta W = \frac{1}{2}\Delta(V) = \frac{1}{2}[\Delta(V_{ee}) + \Delta(V_{en}) + \Delta(V_{nn})] \quad 2.$$

where $\langle V \rangle$ is the average electrostatic potential energy and the subscripts e and n refer to electrons and nuclei. In ethane the experimental barrier is very nearly $\frac{1}{2}\Delta\langle V_{nn} \rangle$, which is merely the barrier one would calculate using bare protons and multiplying by one-half. The quantity $\frac{1}{2}\Delta\langle V_{nn} \rangle$ also compares very well with the experimental barrier height in CH_3SiH_3 , CH_3GeH_3 , CH_3OH , and $\text{CH}_3-\text{C}=\text{C}-\text{CH}_3$, but it must be noted that the calculations are fairly sensitive to the equilibrium H-H distances. The first question is: why are such good results obtained when $\Delta\langle V_{ee} \rangle$ and $\Delta\langle V_{en} \rangle$ are ignored? Secondly: how can the treatment be *reasonably* extended to substituted ethanes, such as $\text{C}_2\text{H}_5\text{X}$ where X is no longer a proton?

Several new papers have appeared on the interpretation of the microwave spectra of molecules having one or more symmetric internal rotors. Herschbach (58), with the aid of his "bootstrap" technique, has extended to fourth order the tables of perturbation coefficients needed in Wilson and co-workers' (59) analyses of the rotational spectra of molecules containing a single internal rotor. These tables can also be applied in perturbation calculations on double internal rotor molecules. The Hamiltonian for overall and internal rotation in these double internal rotor molecules is somewhat complicated because of the presence of two internal degrees of freedom. However, standard symmetry principles can be applied in order to determine in advance the symmetry and degeneracy (other than accidental) of energy levels, the selection rules for absorption of radiation, the nuclear spin statistical weights, etc. Myers & Wilson (60), using group theoretical methods, have determined these symmetry properties for molecules that contain two equivalent internal rotors and have C_{2v} or C_2 symmetry when the internal rotors are rigidly fixed in their equilibrium conformations. For this class of molecules the Hamiltonian is invariant to a set of 36 operations, which constitutes a group isomorphous with the direct product of C_{2v} and C_{3v} . Examination of the symmetry properties of the torsional and rotational wave functions reveals that rotational transitions in the ground torsional state should be split into four components, with relative intensities that are readily computed. These quadruplets have been seen by Swalen & Costain (61) in the microwave spectrum of acetone, but more often than not, two of the components cannot be resolved (62, 63, 64) and the transitions appear as triplets. This will occur, as Wilson & Myers point out, whenever certain terms coupling the two internal rotors can be neglected and the barrier to internal rotation is sufficiently high. Detailed calculations of the energy levels for internal and overall rotation, omitting coupling terms between the two internal rotors, have been performed on several molecules (61, 64, 65) with quite satisfactory results.

NUMERICAL CALCULATIONS

The utilization of high speed computers in solving the numerical problems of rotation and vibration spectroscopy has been spurred on by the increased availability of electronic calculating machines. Overend & Scherer (66 to 71) have produced a series of papers on the evaluation of Urey-Bradley

force constants via a numerical iteration method. The procedure they follow has been known for quite some time (72, 73). One begins with some reasonable initial set of guesses for the force constants and, on the basis of these guesses, calculates a set of λ 's, where $\lambda = 4\pi^2\nu^2$ and ν is the vibrational frequency. These calculated λ 's will generally be different from the observed λ 's, but hopefully not too different, so that an improved set of force constants will be generated by the matrix relation

$$\lambda_0 - \lambda^{(i)} = J(f^{(i+1)} - f^{(i)}) \quad 3.$$

Here $\lambda_0 - \lambda^{(i)}$ and $f^{(i+1)} - f^{(i)}$ are column matrices; the former contains the differences between observed and calculated λ 's as elements, while in the latter matrix, $f^{(i)}$ and $f^{(i+1)}$ represent, respectively, the initial and improved guesses for the force constants. The Jacobian J of partial derivatives, relating the λ 's and the force constants is evaluated at the point determined by the initial guesses. Naturally, the key step in the entire calculation is determining the elements of J , and this is done by means of first order perturbation theory, with the result that

$$\left[\frac{\partial \lambda_m}{\partial f_{pq}} \right]_{(i)} = L_{pm}^{(i)} L_{qm}^{(i)} (2 - \delta_{pq}) \quad 4.$$

where $L^{(i)-1} G F^{(i)} L^{(i)} = \lambda^{(i)}$, and δ_{pq} is the Kronecker delta. Once the improved set of force constants have been obtained, they, in turn, can be used as a set of initial guesses, and the process repeated until the force constants converge to fixed values. Clearly, if the number of observed frequencies exceeds the number of unknown force constants, the force constants are overdetermined. To take into account all of the data, a least squares treatment is necessary and the relation $\Delta\lambda = J\Delta f$ (i.e., Eq. 3) should be replaced by

$$J^\dagger W \Delta\lambda = J^\dagger W J \Delta f \quad 5.$$

where W is a somewhat arbitrary diagonal weight matrix and J^\dagger is the transpose of J . The arbitrariness in W reflects a similar arbitrariness in selecting which error to minimize in the least squares treatment. For example, if one weights all the observed frequencies equally and chooses to minimize the percentage error in these frequencies, then $W \propto \lambda^{-2}$; on the other hand, the absolute error in the frequencies is minimized by choosing $W \propto \lambda^{-1}$. Furthermore, for any one of a variety of reasons, it might be still better policy to give unequal weights to different observed frequencies.

When there are fewer observed frequencies than force constants it becomes necessary either to constrain some of the force constants to fixed values or introduce extra-curricular information. It has been suggested by Mills (74, 75) that such extra information might conceivably come from Coriolis coupling constants and centrifugal distortion constants. With this view in mind he has developed a first order perturbation procedure for obtaining the Jacobians relating the Coriolis ξ 's and centrifugal distortion τ 's to the unknown force constants. However, in actual practice, centrifugal distortion τ 's are usually so poorly determined (76, 77, 78) that their value in deter-

mining accurate force constants is somewhat questionable. This leaves the Coriolis zetas, which may occasionally complement the frequency data but are often relatively independent of the force constants (79) and contain unknown contributions attributable to anharmonicities.

Overend and Scherer's calculations were initiated for the purpose of determining the transferability of Urey-Bradley force constants. As to this point no definite conclusions can be drawn, the transferability of force constants evidently varying from one force constant to another and depending upon the particular series of compounds studied. However, in the course of these investigations, several facts were uncovered that, although already known to spectroscopists, deserve to be reemphasized. Among these we list the following: (a) certain force constants cannot be determined accurately from vibration frequencies even when complete data on isotopic substitution are available; (b) ignoring anharmonicities has a significant influence on calculated potential constants and may or may not obscure trends; (c) one must be circumspect in ascribing changes in "group" frequencies as being due to changes in one particular force constant or in one particular chemical bond; in general, variations in all the force constants as well as mass and structure alterations must be taken into account; and (d) the uncertainty in a particular potential constant is often intimately related to the uncertainty in at least one other force constant.

The coming of age of the electronic digital computer has also caused the blossoming forth of several papers on the numerical evaluation of rigid asymmetric rotor energy levels. It is well known (80) that these energy levels can be found as the eigenvalues of certain real, symmetric, tridiagonal matrices, in which tridiagonal is taken to mean that the only non-zero elements occur on the diagonal and immediately above and below the diagonal. Thus the methods devised for finding rigid asymmetric rotor energies can also be applied to finding the eigenvalues of any real symmetric tridiagonal matrix. Moreover, the range of applicability includes all real symmetric matrices, for these can easily be reduced to tridiagonal form by the Givens-Jacobi method (81).

Swalen & Pierce (82), following a suggestion by Posener (83), have modified the classical continued fraction approach by introducing a Newton-Raphson iterative procedure (Posener's Eq. 61). This procedure requires the derivative of the continued fraction with respect to an assumed eigenvalue. Posener obtains this derivative approximately, but Swalen & Pierce show that it can be evaluated exactly with little extra computation. Without the aid of the Newton-Raphson approximation, the continued fraction calculation would converge more slowly or, in some cases, perhaps not at all. It is also important, in order to speed up convergence and avoid skipping over certain eigenvalues, to choose the "best possible development" of the continued fraction. In an n^{th} order problem one may develop the continued fraction about any one of the n diagonal matrix elements. If the k^{th} original basis function makes the largest contribution to the true eigenfunction, then

it is most reasonable to assume that the "best development" will be about the k^{th} diagonal matrix element. According to this criterion Swalen & Pierce show how the "best possible development" can easily be found if a fairly good approximation to the true eigenvalue is available.

A different approach to the rigid asymmetric rotor eigenvalue problem has been prescribed by Bennett, Ross & Wells (84). They employ the quotient-difference algorithm of Rutishauser to reduce the tridiagonal matrix to a di-diagonal one where the elements on the diagonal are the rigid asymmetric rotor eigenvalues arranged, in almost all cases, in decreasing numerical order.

A direct preliminary comparison (85) of the two methods reveals that the quotient-difference algorithm is faster by approximately a factor of two. However, the comparison was made with the approximate Newton-Raphson procedure (i.e. Posener's), which is expected to be somewhat slower than the exact procedure of Swalen & Pierce. Then, too, the proper choice of development of the continued fraction was quite possibly not taken into account in this comparison since there is no mention of it. The main difference between the two approaches is that continued fractions allow for the individual calculation of any selected eigenvalue, whereas the quotient-difference algorithm produces eigenvalues in numerical order. However, if continued fractions are to be used in calculating degenerate or nearly degenerate eigenvalues then the Newton-Raphson procedure should be replaced by the "entrapment" method described by Pierce (85). Essentially what one does in that case is define a recursive sequence of continued fractions and then count the number of positive and negative terms in this sequence when some arbitrary value γ is substituted into the continued fractions. This gives the number of eigenvalues $P_n(\gamma)$ that are less than γ , according to the formula

$$P_n(\gamma) = \frac{1}{2}[n + n_+(\gamma) - n_-(\gamma)] \quad 6.$$

where n is the total number of eigenvalues and $n_+(\gamma)$, $n_-(\gamma)$ are the number of positive and negative terms in the sequence of continued fractions. In this manner it is trivial to "localize" eigenvalues within an interval $\Delta\gamma$, which in principle can be made as small as desired.

The problem of the energy levels of a slightly asymmetric rotor has recently been heavily belabored (86 to 89). As it now stands, tabulated values are available up to and including the seventh-order approximation for $J \leq 51$, and if an IBM 650 computer, or equivalent, is handy the calculations can be extended to any desired degree of approximation for $J \leq 100$ (86).

DOUBLE MINIMUM POTENTIALS

Considerable interest has centered of late about vibrations with a double minimum potential. Such diverse vibrations as the bending of an almost linear triatomic molecule, the puckering of a slightly puckered ring compound, and the stretching of a hydrogen bond fall into this category. The spectroscopic consequences of a double minimum bending potential for a

slightly bent B—A—B (C_2 symmetry) molecule have been investigated theoretically by Thorson & Nakagawa (90). They consider a double minimum bending potential of the form

$$V(r) = \frac{1}{2}k_r r^2 + \frac{K_B}{(C^2 + r^2)}, \quad (r = R_0\alpha) \quad 7.$$

where α measures the angular deviation from linearity and R_0 is the equilibrium A—B bond length. By varying the parameters K_B and C , a potential hump for the linear configuration of arbitrary height and width may be obtained. A very high potential barrier corresponds to the limiting case of a "bent" molecule, while a zero barrier with large curvature at $r=0$ corresponds to the limiting case of a linear molecule. Potential functions intermediate between these two extremes (and particularly when the barrier height is comparable to the harmonic vibrational frequency) define what is meant by a "quasi-linear" molecule. Assuming that the amplitude of the bending vibration is much larger than the amplitude of either of the stretching vibrations, Thorson & Nakagawa (90) have derived an approximate Hamiltonian for the quasi-linear B—A—B molecule. In the zeroth order approximation this Hamiltonian depends upon r in two ways. One is through the potential energy $V(r)$ and the other is through the explicit dependence of the least moment of inertia upon r . The energy levels for bending and rotation about the least axis of inertia were calculated for two values of k_r (see Equation 7 above) and for different sets of K_B and C , subject to the restriction that the mean square displacement from the linear configuration corresponds approximately to an B—A—B bond angle of 150 degrees. Even when the barrier is quite low, the energy pattern is similar to that of an ordinary "bent" molecule. Each bending vibrational level has associated with it a series of rotational levels that overlaps the series arising from the next highest vibrational level. The dipole intensities, on the other hand, are more closely akin to those of a linear molecule. Let V and n represent, respectively, the bending vibrational quantum number for the linear and for the bent or quasi-linear molecule, and let ℓ be the angular momentum quantum number for rotation about the least axis of inertia. The selection rule for infrared absorption by a linear molecule is $\Delta V = +1$ and $\Delta \ell = +1$ or -1 . Transitions with $\Delta \ell = +1$ correspond to the pure rotation spectrum ($\Delta n = 0$, $\Delta \ell = +1$) of a bent or quasi-linear molecule and are predicted to be quite intense. The $\Delta \ell = -1$ transitions, calculated to be considerably weaker, correlate with the P -branches of the bending fundamental, i.e. $\Delta n = +1$, $\Delta \ell = -1$ transitions of the bent or quasi-linear molecule. The R -branches of the bending vibrations, i.e. $\Delta n = +1$, $\Delta \ell = +1$, are associated with the "forbidden" $\Delta V = +3$, $\Delta \ell = +1$ transitions of a linear molecule and hence are expected to be very weak. Thus the salient feature of the far infrared spectrum of a quasi-linear molecule will be the strong absorptions caused by pure rotation ($\Delta n = 0$, $\Delta \ell = +1$) that may easily overlap and obscure the weaker P -branches of the bending fundamental. This has been found to be the case in

disiloxane [Aronson, Lord & Robinson (91)]. The stretching vibrations will be affected, too, by the unusual shape of the bending potential. Both the kinetic energy associated with the stretching motions and the anharmonic cross terms between bending and stretching depend upon the mean square bond angle. This quantity will vary rather widely with different values for the quantum numbers n and ℓ , thus giving rise to multiple components for the stretching vibrations. This qualitative conclusion, too, has been confirmed for the asymmetric stretching vibration of disiloxane (91). The symmetric stretch, of course, is "forbidden" in a linear molecule and is apparently too weak to be seen in the infrared. The spectral data that are presently available are insufficient for quantitative characterization of the double minimum bending potential of disiloxane.

On the other hand, a rather complete microwave study by Gwinn and co-workers (92, 93) and an infrared study by Danti, Lafferty & Lord (94) of the ring-puckering vibration of trimethylene oxide permits several important quantitative conclusions (93) about the double minimum potential for this vibration to be drawn. Rotational transitions due to trimethylene oxide molecules in the ground, 1st, 2nd, 3rd, and 4th excited states of the ring bending vibration have been seen in the microwave spectrum. The bending vibrational states are degenerate in the limit of a high potential barrier at the planar configuration, but are split when the barrier is lowered. Since the statistical weights of the two split levels are different, it can be decided whether or not the levels are degenerate merely by comparing the relative intensities of a rotational transition with its vibrational satellites. From the microwave intensities it can be concluded that the puckering vibrational levels of trimethylene oxide are non-degenerate. Furthermore, the 1st excited state is $60 \pm 20 \text{ cm}^{-1}$ above ground and the splitting between the 1st and 2nd excited states is $110 \pm 20 \text{ cm}^{-1}$. More accurate data on the location of these and the higher levels are, however, available from the infrared spectrum. Stark effect measurements (93) verify the conclusion that the bending vibrational states are non-degenerate. In fact, assuming that the ring is bent by 12 degrees, the absence of an anomalous Stark effect due to a dipole component perpendicular to the ring ensures that the splitting between the first two inversion levels is at least 2.5 cm^{-1} . If the splittings were somewhat larger than this, the effective rotational constants for the two components of the inversion doublets would be different enough, at least in higher vibrational states, to give rise to observably different rotational frequencies. The fact that the rotational transitions in different excited bending states are not doubled, together with the intensity and Stark effect data, gives strong evidence that the vibrational states are not degenerate or nearly degenerate. These results indicate a low potential barrier to ring-inversion.

In the absence of strong Coriolis effects the effective rotational constants in the i^{th} vibrational state of the ring-puckering mode are

$$(\mathcal{R}_{ij})_{ii} = \mathcal{R}_{ij}^0 + \beta_{ij}^{20}(Q_1^2)_{ii} + \beta_{ij}^{40}(Q_1^4)_{ii} + \dots$$

8.

where Q_1 is the normal coordinate for ring-bending. The variation of the rotational constants with vibrational level can be calculated from an assumed potential function for the ring-puckering vibration, which determines the expectation values $\langle Q_1^2 \rangle_{ii}$, $\langle Q_1^4 \rangle_{ii}$; and three experimental points, which determine B_{00}^0 , β_2^{00} , and β_4^{00} . Since five experimental points are available, the validity of the assumed potential function can be tested. It is found that the experimental rotational constants (particularly A) exhibit a peculiar zigzag variation with vibrational level. This zigzag feature cannot be reproduced by a simple anharmonic potential function of the form

$$V(Q_1) = aQ_1^2 + bQ_1^4 \quad 9.$$

However, the zigzagging can be accounted for by the addition of a Gaussian term $ce^{-dQ_1^2}$, which produces a maximum in the potential function at the planar configuration. The presence of a quartic term in the potential function is required in order to explain the frequencies of the hot bands seen in the infrared. By fitting the rotational constants and infrared frequencies, a barrier height of $35 \pm 5 \text{ cm}^{-1}$ was obtained. Since the lowest vibrational level is $8 \pm 4 \text{ cm}^{-1}$ above the top of the barrier, trimethylene oxide is essentially a planar molecule.

A similar situation arises in formamide where the lowest vibrational level for the out of plane wagging of the NH_2 group (the two hydrogens move perpendicular to the plane of the molecule) is found to be just slightly below the potential barrier [Costain & Dowling (95)]. This was ascertained by fitting a Manning (96) three-constant, double-minimum potential to the fundamental wagging frequencies as determined from microwave intensity measurements on the NH_2 , NHD , and ND_2 isotopic species. The distance of the minima from the plane of the molecule as determined by the Manning potential is in accord with the independent structural determination of this distance. Unfortunately only the ground and first excited states of the wagging vibration were seen in the microwave spectrum, and thus a careful analysis of the double minimum potential such as was performed for trimethylene oxide is impossible at present. An interesting point arises in connection with the discovery of the double minimum potential for formamide. In the past, a small positive inertial defect was taken to be evidence for a planar configuration (97) since non-planarity makes a negative contribution to the defect. However, this rule is violated by normal formamide and it was not until deuterium substitution showed an anomalous decrease in the inertial defect that the non-planarity was discovered.

Another vibration, apparently governed sometimes by a double minimum potential, is the stretching of a hydrogen bond; this is discussed rather generally by Barrow (98). Spectroscopic evidence for this includes the splitting of the fundamental (99 to 102) and overtones (103) of the hydrogen stretching vibration; broadening of this vibrational mode in ice by tunneling (104); apparent visible and infra-red absorptions (102) due to the proton transferred species; and nuclear magnetic resonance relaxation studies in solids

(105). The detailed shapes of the double minimum potentials due to hydrogen bonding have not been established as yet.

CONDENSED PHASES

The mechanism of intermolecular coupling of vibrations in molecular crystals is poorly understood. Transition-dipole-transition-dipole interactions have been proposed by Decius (106, 107, 108) and again by Hexter (109). On the basis of this type of interaction Hexter has calculated, by first order perturbation theory, the correlation field splittings of the parallel bands of CH_3Cl . In order to do this he has introduced a vibrational exciton theory that exactly parallels the electronic exciton theory used by Davydov (110), Craig & Hobbins (111), and Fox & Schnepf (112). The splittings, thus calculated, turn out to be considerably smaller than observed unless it is postulated that the dipole derivatives $\partial u/\partial Q_i$ in the crystal are from one to five times larger than those in the gas. Thus far only the gaseous dipole derivatives of CH_3Cl have been measured (113), but Person & Swenson (114) have found from infrared intensities that benzene dipole derivatives decrease, rather than increase, upon crystallization. Dows, too, (115) has found that gaseous dipole derivatives lead to dipolar correlation field splittings for CH_3Cl which are too small. He has proposed that intermolecular coupling can also take place via direct interatomic repulsions. If it is assumed that $\text{H} \cdots \text{H}$ repulsions in crystalline CH_3Cl satisfy a de Boer (116) potential, a significant correlation field splitting arises from these repulsions alone. At the present time it can only be concluded that further speculations into the nature of the intermolecular coupling of vibrations await the accumulation of a larger body of experimental data. With this in mind, Dows (117) has extended his studies on the crystalline methyl halides to include CD_3Cl and CD_3Br .

Swenson, Person, Dows & Hexter (118) have achieved, for the first time, the resolution and assignment of the crystal field splitting of a benzene fundamental. Under high resolution, the degenerate fundamental ν_{20} appears as a singlet at 1039.4 cm^{-1} , plus a partially resolved doublet at 1034.7 and 1032.6 cm^{-1} . The component at 1032.6 cm^{-1} is about twice as intense as either of the other two components and on this basis was assigned as the *b*-axis singlet. There remain the components at 1039.4 and 1034.7 cm^{-1} as members of a correlation field doublet, which, from polarization measurements (119), are respectively the *c* and *a* components of this doublet. The site group and correlation field splittings of the ν_{20} fundamental are thus about equal in magnitude, which is contrary to the idea advanced earlier (120, 121) that the site group splitting should be the larger of the two.

An identical result was found for the ν_{20} fundamental of benzene- d_6 . In mixed crystals of benzene and benzene- d_6 in the ratio 10 to 1 the correlation field splittings of this fundamental disappear and leave only the site group splitting. On the other hand, the correlation field splittings reappear in pure benzene- d_6 and thus enable the two types of splittings to be distinguished.

The mixed crystal method has also been used by Person & Olson (122) to interpret the 705 cm^{-1} band of benzene. Recently (123) this band was assigned as a combination between ν_{11} (687 cm^{-1}) and a postulated low-lying lattice rotational mode at 17 cm^{-1} . However, in a mixed crystal of $1\text{ C}_6\text{H}_6:10\text{ C}_6\text{D}_6$, Person & Olson found that the 705 cm^{-1} and 687 cm^{-1} bands collapsed into a single band at 696 cm^{-1} indicating that these formed a correlation field doublet of ν_{11} .

In further studies on crystalline benzene Swenson & Person have determined, despite formidable experimental problems, both the relative and absolute intensities of the infrared bands (114, 124). All of these bands decrease in intensity upon going from the gas (or liquid) to the solid. However, the decrease varies from band to band. Undoubtedly the explanation lies in a decrease in the magnitude of the dipole derivatives, but the reason for this decrease is not understood. Absolute infrared intensity measurements have also been made on the ammonium ion (125) both in solid solutions of alkali halides and in pure NH_4I . From these measurements approximate bond dipole derivatives and bond dipole moments were obtained. The dipole derivatives correspond to much larger effective atomic charges than do the bond moments and vary considerably with environment. In addition to Ferriso & Hornig's study, there have been several other papers (126, 127, 128) on the spectra of polyatomic ions dissolved in alkali halide lattices, mostly concentrating on frequency shifts.

The infrared spectrum of liquid and solid H_2 taken over a range of *para*-concentrations, and the Raman spectrum of the solid, have been reported by Welsh *et al.* (129, 130). Van Kranendonk, on the basis of his earlier theories (131), has interpreted these solid *para* hydrogen spectra (132). Comparison of theory and experiment yields detailed information about the anisotropic intermolecular forces in solid hydrogen that cause the appearance of the energy bands, and about the rotational and vibrational motions of the molecules in the solid.

In the infrared spectrum of *m*-toluidine and other aromatic amines, Evans & Wright (133, 134) have observed what they describe as a "peculiar effect" and one they believe is of general occurrence. Apparent sharp emission bands occur in the liquid spectrum and are enhanced in the amorphous solid, diminished greatly in CS_2 dilute solution, and absent in the vapor. These bands coincide in frequency with absorptions found in the Raman spectrum of the liquid. In all cases the apparent emission band occurs at or near the frequency of a broad band described as the NH_2 wagging mode. The suggested origin of this effect is a perturbation between a narrow-banded, weakly allowed infrared vibration and the broadbanded NH_2 wag. Due to this perturbation an energy level "hole" is created at the energy of the narrow-banded vibration thus giving rise to a sharp decrease in absorption intensity at this point.

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QUANTUM THEORY: ELECTRONIC STRUCTURE AND REACTIVITY OF LARGE ORGANIC MOLECULES¹

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The quantum-theoretical field of molecular structure is clearly divided into two major parts: one is concerned with the highly accurate, quantitative treatments of small molecules, while the other involves the semi-empirical approximations for large molecules. The gap between the two has become increasingly apparent during recent years (1), to the extent that the two classes of topics may not be surveyed adequately with equal weight. Contrary to the tradition of this series, the present review places a unilateral emphasis on the semi-empirical theories concerning large organic molecules, partly because of the author's preferential interest in them and partly because of his intention to avoid a monotonous description of all of the numerous papers on molecular structure. Thus, the survey of recent developments of the quantitative theory for small molecules may await more competent hands in future years. Moreover, since a limited number of topics are selected for review, even some important papers concerning large organic molecules have been either slighted or neglected. For these omissions the author begs the excuse of conflict in interest.

ELECTRONIC STRUCTURE

The conventional models for conjugated organic molecules, when treated on the basis of quantum theory, are those in which mobile π -electrons are assumed to be completely separated from σ -electrons. Because of the mobile nature of π -electrons, many physico-chemical properties of conjugated compounds have been successfully interpreted by what is known as the π -electron theory. In recent years many additional insights have been gained into the nature of this mobile electron in conjugated molecules. These will be described in the following sections.

Excitation energy and charge distribution.—Efforts at determining or modifying the orbital energies and intramolecular distributions of π -electrons have been attempted by a number of workers, mostly in terms of the linear-combination-of-atomic-orbital (LCAO) molecular-orbital (MO) theory. The π -electron distribution is particularly important for the understanding of chemical behaviors and dipole moments of conjugated molecules, and the orbital energy is a quantity that should be directly related to electronic spectra, ionization potentials, etc.

¹ The survey of the literature pertaining to this review was concluded in November 1960.

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In the simplest form of the LCAO-MO method by Hückel (2), the π -electronic repulsion terms are averaged and suppressed into the so-called one-electron effective Hamiltonian. The only energy integrals appearing there are the effective Coulomb integrals and resonance integrals. Overlap integrals between atomic orbitals may or may not be included according to the nature of the problem. In most cases, resonance integrals between non-neighboring atoms are neglected. Despite this highly-simplified formalism, the Hückel method is capable of elucidating roughly many chemical and physical properties of conjugated molecules (3).

The chief disadvantage of the Hückel theory is the fact that it does not give a proper account of spectroscopic properties (4). Moreover, the theory predicts the same ionization potentials for all radicals of odd-alternant type even when overlap integrals are included for calculation, whereas, for example, the experimental ionization potentials for methyl, allyl, and benzyl radicals are not identical and are known to be 9.88, 8.22, and 7.76 eV, respectively. Undoubtedly, these defects of the Hückel theory arise from a neglect of electronic repulsion terms.

Goeppert-Mayer & Sklar (5) first included explicitly the π -electronic repulsion terms in the calculation of π -orbital energies of benzene. In this treatment the antisymmetrized determinants were used for π -electronic wave functions and all energy integrals including electronic repulsion integrals were evaluated theoretically with Slater's $2p\pi$ atomic orbitals. The technique is now referred to as the method of the antisymmetrized products of molecular orbitals.

Later, Roothaan (6) developed a general theory of the "self-consistent field" for the LCAO-MO's [the method of self-consistent field (SCF) LCAO-MO], and Craig (7) emphasized the necessity of including the "configuration interactions."

These purely theoretical molecular orbital theories provided an excellent explanation for the electronic spectra of conjugated molecules. In these non-empirical methods, however, all quantities entering the formulas are computed theoretically in terms of nuclear distance and effective nuclear charge of an atom for a π -electron. The procedure involved is too laborious for the purpose of predicting molecular properties. What was needed was thus a less laborious, yet equally useful approximation.

A promising approach along the above-mentioned line was initiated independently by Pariser & Parr (8) and by Pople (9), both in 1953. Excellent interpretative descriptions of these approaches can be found in reviews by Parr & Ellison (4) and by Pople (10) and also in a recent book by Daudel, Lefebvre & Moser (11). Here it will suffice to mention that both methods are modifications of Roothaan's self-consistent field theory; they are simplified by introducing a number of reasonable semi-empirical ways of evaluating various integrals and thus may be regarded as semi-quantitative supplements to the simple Hückel method through the inclusion of electronic repulsions. Therefore, these semi-empirical methods might well be referred to as the

"generalized Hückel method (4)" or "SCF-like LCAO-MO method."

In the original forms of the above SCF-theories, the effect of changes in the electronic structure of one set of electrons on those of another set of electrons was not taken into account. Parks & Parr (12) fully investigated the limitation of the assumption of separability of electron pairs in molecules and provided a procedure for obtaining best orbital descriptions for the separated electron-pairs. The theory of separated electron pairs, including configuration interaction, was then applied by the same workers (13) to excitation and ionization of formaldehyde as an example of the treatment of unsaturated molecules with lone-pair electrons. For $n \rightarrow \pi^*$ transitions the principle of the treatment was briefly as follows: Excitation of an n -electron to a π^* -orbital induces a change in environment for σ -electrons. The wave functions for the σ -electrons must then be adjusted accordingly, followed by a change in environment for the excited π -lone-pair system. Readjustment of the wave function for the π -lone-pair system causes further readjustment of the sigma wave function, and so on until both wave functions become mutually consistent. The calculated energy value for singlet-triplet $n \rightarrow \pi^*$ excitation of formaldehyde was in the range of 3.41 to 3.94 ev according to the characterization of calculation procedure, to be compared with the experimental value of 3.02 ev. The problem of correlation correction (14, 15) and the change in bond polarity because of the sigma reorganization upon excitation were also discussed in the same paper (13).

The excitation in formaldehyde has also been treated by Brown & Heffernan (16), with a different scope from that of Parks & Parr (13). It has been customary in the SCF method to use a fixed value for the effective nuclear charge Z_p of each atom p in a molecule. Since Z_p is an index of the electronegativity of an atom p , it is to be expected that the Z_p is dependent on the π -electron density on the atom p . Thus, in addition to the usual functional dependence of the SCF matrix elements upon the charge distribution, the electronic repulsion integrals $(pq|rs)$ and penetration integrals $(r:pq)$ become functions of the electron density through their dependence on the nuclear charge. Brown & Heffernan employed, for conjugate systems, the Pople-type generalized Hückel theory, defining the matrix elements as

$$F_{pp} = -I_p + \frac{1}{2}P_{pp}(p|p) + \sum_{q \neq p} (P_{qq} - 1)(p|q) - \sum_r (r:p|p) \quad 1.$$

$$F_{pq} = \beta_{pq} - \frac{1}{2}P_{pq}(p|q) \quad 2.$$

and relating Z_p to P_{pp} by

$$Z_p = Z_p^0 - 0.35P_{pp} \quad 3.$$

where P_{pp} and P_{pq} are the π -electron density on an atom p and the π -bond order of a bond p - q , respectively, and Z_p^0 is the effective nuclear charge of the atom p in the atomic state, which is determined by Slater's rule. The valence-state ionization potential I_p is also regarded as varying with P_{pp} . Thus, in this SCF-like procedure, the iterative computation should lead to self-consistent values of Z_p as well as of P_{pp} . The technique may, therefore,

be termed as "the self-consistent electronegativity method" or rather "the variable electronegativity (VE) SCF-like LCAO-MO method."

It is readily supposed that the concept of the variable electronegativity is especially practical for conjugated molecules of non-uniform charge distribution. The method has been applied not only to formaldehyde (16) but also to various N-containing aromatic compounds and their positive or negative ions (17 to 21) and to azulene (22). The main conclusions derived from this series of investigations by Brown & Heffernan (16 to 22) are summarized as follows: (a) Dipole moments of conjugated molecules calculated by the VESCF method without invoking σ -bond polarities are in marked agreement with experimental values, and subsequently the assumption of an unpolarized σ -core in hetero-conjugated molecules seems to be more reasonable than is widely believed. (b) The resonance integral for a carbon-heteroatom bond, which was evaluated by comparison of the VESCF theory with experiment for a $\pi \rightarrow \pi^*$ excitation in a hetero-conjugated molecule, reproduces the energies of other $\pi \rightarrow \pi^*$ excitations and singlet-triplet $n \rightarrow \pi^*$ excitations in the molecule as well as any other SCF theory does. (c) The estimates of ionization potentials are always too great by a few eV, as is generally the case in the usual self-consistent field theories for conjugated molecules. (d) It is desirable to estimate the Coulomb parameters for heteroatoms in the simple Hückel method so that the parameters give the same results for the charge distribution as found in the VESCF calculations.

Another semi-empirical method of approach for conjugated systems has been suggested by Julg (23), who emphasizes the importance of taking into consideration the correlation among electrons (14). That is, the electron repulsion term appearing in the Hamiltonian operator should be $f^2(r_{\mu\nu})/r_{\mu\nu}$ instead of $1/r_{\mu\nu}$ hitherto considered, where $f(r_{\mu\nu})$ is a function of the distance $r_{\mu\nu}$ alone and tends to zero as the two electrons, μ and ν , approach each other. Therefore, the bielectronic probability is no longer the product of the mono-electronic probabilities $\chi^2(\mu)$ and $\chi^2(\nu)$ but is expressed as $\chi^2(\mu) \cdot \chi^2(\nu) \cdot f^2(r_{\mu\nu})$, where χ is the atomic orbital function. The introduction of this correlation correction into the self-consistent field LCAO-MO theory turns out to be a necessity in evaluating the new repulsion integrals of the general type

$$\iint \chi_p(\mu) \chi_q(\nu) \frac{f^2(r_{\mu\nu})}{r_{\mu\nu}} \chi_r(\mu) \chi_s(\nu) d\tau_\mu d\tau_\nu \quad 4.$$

The exact term of the $f(r_{\mu\nu})$ still being unknown, Julg has devised empirical rules for evaluating the one- and two-centered integrals alone, by varying the nuclear charge Z . The method was applied with success to ethylene (23), *trans*-butadiene (23), hexatriene (24), benzene (23), formaldehyde (25), and fulvene (26), giving good agreement between theory and experiment of dipole moments and excitation energies.

The effect of paramagnetic molecules P on singlet-triplet excitations of conjugated molecules M was interpreted by Hoijsink (27), assuming a weak exchange interaction between P and M. A perturbation theory was proposed

by McConnell (28) to estimate the ground-state singlet-triplet splittings in various π -biradicals with bridge structures.

The $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitations in N-containing heterocyclic molecules have continuously received attention by Anno & Sadó (29, 30) on the basis of a semi-empirical antisymmetrized-product-of-molecular-orbital (ASMO) method (31, 32) and by Brinen & Goodman (33) utilizing the Pariser-Parr type method (8). The effect of electron-releasing substituents on the ionization potential and $\pi \rightarrow \pi^*$ excitation energy of benzene was investigated by I'haya (34, 35), using the single configuration LCAO-MO method (36) and Pariser-Parr's approximation (8) for electronic interaction. In I'haya's papers, however, emphasis was placed on the method of determining the empirical parameters for the substituents.

Ionization potential.—It has been customary in usual molecular orbital theories to assume that for a closed-shell configuration, the ionization potential is equal to $-\epsilon_n$, where ϵ_n is the energy of the highest filled orbital in a molecule [Koopman's theorem (37)]. However, when this theorem is combined with the non-empirical SCF theory for conjugated molecules, the calculated ionization potentials are usually greater than the experimental data. This discrepancy is believed to arise from a neglect of the following factors (38): (a) The effect of π -electron ionization on the σ -framework; (b) changes in the $2p\pi$ basis functions on ionization; and (c) changes in the π -molecular orbital through construction of a new self-consistent field for the ionized states. Hoyland & Goodman (38) attempted an empirical analysis on the first two factors, by assuming that the changes of σ -electronic energy, valence-state ionization energy, and π -electronic repulsion integrals associated with $2n$ atom p are proportional to the change in π -electronic density P_{pp} through a linear dependence of Z_p on P_{pp} . Estimating the three proportionality constants by comparing theory and experiment for the ionization potentials of benzene, ethylene, and acetylene, they calculated the potentials for *trans*-butadiene, *trans*-hexatriene, styrene, naphthalene, anthracene, and phenanthrene. The values thus obtained are about 2 ev smaller than those derived with direct application of Koopman's theorem and are in fair agreement with experiment. Although the treatment is empirical in nature, the attempt is noteworthy in that the results clearly indicate an essential importance of "the after-effect," i.e., the stabilization of conjugated molecules upon ionization. It should be noticed here that the basic principle underlying this modification is equivalent to the concept of variable electronegativity by Brown & Heffernan (16 to 22), although for π -ionization the latter workers ignored the σ -stabilization and stuck to Koopman's theorem.

The above "after-effect" seems important for a better understanding of ionization potentials even when the calculation of orbital energies is much cruder. In the simple Hückel method, the relative magnitudes of ionization potentials of aromatic conjugated compounds are well correlated with the heights of the highest occupied molecular orbitals (39). As already mentioned, however, the correlation fails to hold for conjugated radicals. As to this in-

adequacy of the simple Hückel method, Streitwieser (40, 41) demonstrated that a simple modification of the Hückel theory gives a consistent relation between experimental ionization potentials and calculated orbital energies for both conjugated molecules and radicals. His modification lies in the use of the " ω -technique" for calculating the π -orbital energies of positive ions. That is, the total π -electronic energy of a positive ion formed on ionization is obtained after altering the Coulomb integrals of individual carbons in proportion to the net positive charge associated with each carbon, the proportionality constant being $\omega\beta$. This technique has previously been used by several workers (42, 43, 44) to obtain charge distributions in conjugated molecules. Introduction of the ω -parameter obviously causes a heightening of the coulombic attraction between a π -electron and the effectively more electronegative carbon atom. Alternatively, it was shown by Streitwieser (41) that the ω -approximation bears a formal relation to Pople's generalized Hückel theory with additional simplifying approximations for empirical parameters; electron repulsion with distant atoms is treated as an average effect. Therefore, one can conclude that the improvement found by Streitwieser for the relation between ionization potential and electronic structure of conjugated molecules and radicals is attributable to the inclusion of the third supplementary factor for Koopman's theorem, mentioned in the last paragraph.

The same technique as used for conjugated molecules and radicals was further applied to alkanes by Streitwieser, assuming localized pseudo- π -orbitals for CH_2 and CH_3 groups in alkane molecules and a delocalized positive charge over the entire alkane cations. In spite of this artificial device and the inconsistency involved in the assumption, it is interesting to note that the calculated energy differences between alkane molecules and cations satisfy the same linear relation to ionization potentials as that obtained for the case of conjugated molecules. The ionization potentials of a large variety of alkanes predicted by this method agree with experimental data almost as satisfactorily as those calculated by several other workers (45 to 48) using different empirical methods.

Large carbon molecules have also received attention in recent years. Peacock & McWeeny (49) applied the self-consistent field LCAO theory to the graphite π -band as a natural limit of aromatic hydrocarbons and obtained 4.0 eV and 222.7 kcal./mole as the work function of graphite and the π -electron energy of carbon atoms in graphite, respectively. These calculated values compare with the experimental value of 4.3 eV and with the calculated values of 205.8 kcal./mole in benzene and 188.9 kcal./mole in ethylene. Pitzer & Clementi (50) utilized the simple Hückel method to obtain various kinds of thermodynamic data as well as conjugation energies of large linear carbon molecules.

Scale parameter.—In previous sections the importance of the use of variable Z -values for atomic $p\pi$ -orbitals has been mentioned concerning semi-empirical calculations of charge distributions and ionization potentials of conjugated molecules. This is a natural consequence of the general variational principle in quantum theory.

Since the original non-empirical energy calculation accomplished by Goeppert-Mayer & Sklar (5), almost all subsequent non-empirical studies on the π -electronic energy levels of conjugated hydrocarbons have been based on the value of 3.18 as the effective nuclear charge Z for the $2p\pi$ -orbital function of the valence-state carbon atom. However, because there is no unique procedure for determining the value of Z for atomic orbitals in π -electronic systems, one must re-examine the computed π -electronic energies of conjugated molecules according to the variational principle for the scale parameter Z of carbon orbitals. The re-examination was first made by Shull & Ellison on benzene (51).

Recently, Stewart (52) has computed non-empirically the energies of the π -electron levels of benzene over a wide range of Z -values without invoking Goeppert-Mayer & Sklar's W_p approximation (5, 51, 53, 54, 55). The results show a remarkable dependence of the calculated energy levels on Z with either the Sklar approximation (56) or the Mulliken approximation (57) for core-attraction integrals and three- and four-centered repulsion integrals; in the region around $Z = 3.18$, a change of only 1 per cent in Z induces a change in the ground-state total π -electronic energy by about 1.5 eV, and much the same is true for the excited states. Although in Stewart's calculation the optimum value of Z appears to be near 2 for both the ground and excited states (it should be noted here that the value of $Z = 2$ is unusually small for the ground state in contradiction to the general cognizance that the Z for the lowest molecular configuration should be larger than that for a free atom), the excitation energies calculated around this Z -value are very much dependent on the approximation formula used for the evaluation of three- and four-centered repulsion integrals. Even in ethylene (58), which has the simplest π -electron system and contains no room for the appearance of the multi-centered integrals for π -electronic repulsions, the excitation energies are not obtained with any degree of reliability when σ - π interaction (59 to 62) is taken into account in combination with variational procedure for both Z_σ and Z_π . Stewart (58) thus concludes that there is little justification for carrying out elaborate non-empirical calculations to obtain such slightly quantitative values of energy levels, and still less justification for using these values in the analysis of electronic spectra. This pessimistic view seems to be stimulating further elaborations including precise treatments of the whole σ - π systems, use of correct forms of atomic basis functions, and explicit evaluations of the three- and four-centered integrals.

The possibility of the orbital contraction of atoms in molecules is expected to be larger for a d -orbital than for s - and p -orbitals in view of the larger radial function for the former. According to Maeda's model calculations (63), the contraction of a $3d\pi$ -orbital of the sulfur atom in thiophene is such that the energy of the $d\pi$ -electron in the perturbing coulombic field of two carbon cores (each with a positive charge of 3) is minimum when the effective nuclear charge is almost two electronic units larger than that obtained by Slater's rule, whereas both $2p$ - and $3p$ -orbitals are little affected by the same perturbing field. As a result, the overlap between the $3d\pi$ -orbital of

the sulfur and the $2p\pi$ -orbital of the neighboring carbon is enlarged so that $d\pi-p\pi$ bonding and $p\pi-p\pi$ bonding become equally probable for the S—C π -bond formation. The participation of the $d\pi$ -orbital in the formation of the $d-p$ hybrid orbital in sulfur is thus considered to be largely probable, as first suggested by Craig & Magnusson (64).

Bond nature.—The relation between bond length and bond order in conjugated molecules has been dealt with by several authors on the basis of the simple Hückel theory [N-containing heterocyclic compounds by Lofthus (65); oxamide and other amides by Wagner (66); carbon—oxygen bonds by Pilar (67); and nitrogen—oxygen bonds by Jonathan (68)]. The π -bond order of B—N bonds in a borazole ring was estimated to be about 0.45 by comparisons between theory and experiment of the ratio of the diamagnetic anisotropy of borazole to that of benzene [Watanabe, Ito & Kubo (69)]. Most of these authors have paid special attention to the assignment of parametric values to the Coulomb integrals for the electronegative heteroatoms involved. The problem of bond alternation in long polyenes (72 to 76) has been treated further by Salem & Longuet-Higgins (70) and by Tsuji, Huzinaga & Hasino (71).

Free-electron theory.—Somewhat neglected recently is the application of the free-electron method to conjugated molecules. The principal factor preventing the development of the free-electron molecular-orbital (FEMO) theory is the difficulty of including electronic repulsion in the calculation; all electronic repulsion energies turn out to be infinite if the electrons are assumed to move one-dimensionally. In order to cope with this difficulty, some devices have already been designed for the electron-interaction operators by Araki & Araki (77), Araki & Murai (78), and Ham & Ruedenberg (79). However, these devices required the introduction of new parameters, which can hardly be justified theoretically. Nevertheless, it should be noted that they have brought the free-electron molecular-orbital theory up to a level equivalent to the generalized Hückel method. The FEMO theory, including configuration interactions, is as useful as the generalized Hückel theory for interpretation of electronic spectra of conjugated molecules, as has been exemplified for aromatic hydrocarbons (80) and for some of the non-alternant and even-alternant hydrocarbons (81).

In the most common form of the free-electron model, all the π -electrons are assumed to move with complete freedom. In the field of constant potential, only the one-dimensional motion of electrons along the conventionally assumed bond structure plays a role in determining electronic structures. The two other translational degrees of freedom, being frozen to the ground states (82), serve only to give a slight periodic sway of small constant energy to the one-dimensional motion. However, if the free electrons are treated as if they were in the field of core potentials arising from the nuclear charges of atoms constituting molecular skeletons, then the linear motion might be affected more seriously than hitherto considered. This point was investigated by Kuhn *et al.* for the cases of symmetric polymethine ions (83) and of poly-

enes and polyacetylenes (84). For a simple comparison, they assumed three different potential models: (a) the one-dimensional constant-potential model; (b) the one-dimensional wave-shape potential model; and (c) the two-dimensional potential-trough model. Comparison of eigenvalues and eigenfunctions solved for these three potential models showed that the wave functions resulting from models (a) and (b) gave fairly good approximate shapes of the corresponding two-dimensional wave function along the zigzag line of the carbon chain and that the positions of corresponding energy levels resulting from the three models agreed surprisingly well. In a more elaborate case for polyacetylenes, where a three-dimensional potential field was set up by the superposition of the coulombic potentials of carbon nuclear charges, the computed wavelengths of the first electronic excitations were somewhat smaller than, but still in satisfactory agreement with, the observed data. It is rather surprising, however, that the simple sine-curve potential model is the best of all models assumed. This finding may be rather fortuitous, and discrimination of the merits of different models will not be possible at the present stage. Yet, it now seems possible to at least conclude that including the bond-alternating nature in the potential function improves the one-dimensional model of free-electron molecular-orbital theory for long polyenes to an appreciable extent.

Spin density.—Another important family of recent applications of quantum theory to conjugated molecules is seen in the study of electron-spin resonance, which is a topic to be covered by Prof. Weissman in a separate chapter of this volume. The hyperfine interaction a_H between the nuclear and electron spins of aromatic hydrocarbon radicals or ions has generally been assumed proportional to the unpaired π -electron spin density ρ at the carbon atom of the C—H bond. The relation $a_H = Q\rho$, where Q is a hyperfine coupling constant, has been scrutinized theoretically by McLachlan, Dearman & Lefebvre (85). McLachlan (86) utilized the valence bond theory to obtain the spin density distribution in twisted dimethylmethyl radical. Using the method of alternant molecular orbitals (87), Lefebvre, Dearman & McConnell (88) calculated the spin densities in odd-alternant hydrocarbon radicals and found that the spin densities at the unstarred positions are negative in sign, in agreement with the general proof presented by McLachlan (89) on the basis of the valence bond theory as well as the SCF-MO theory.

REACTIVITY.

The study of reactivities of large organic molecules is one of the principal aims of quantum theory. Because of the formidable complexity of organic reactions, it is inevitable that one focuses theoretical attention on the most significant factor for particular reactions and adopts the most suitable reaction model that is simple enough to be manageable, yet detailed enough to represent the essential features involved in the chemical process.

Reactivity index.—The major concern of the quantum-theoretical investigation of organic reactivities has been to give a simple reactivity index with

which relative reactivities of the same group of organic compounds or of the different core positions in a given molecule can be explained as successfully and widely as possible. Since the organic molecules of major interest are those containing π -electrons, most of the work in this field has been directed to investigating the nature of the π -electrons that play an exclusive role in governing the reactivity of these compounds, i.e., conjugated molecules. Reactivities of saturated compounds are occasionally dealt with by a mobile σ -electron model analogous to the π -electron model for conjugated molecules. In all cases, the reactivity indices which correspond to the assumed reaction models have been formulated and computed according to the simple Hückel theory, the most primitive form of the LCAO-MO theory.

For the quantitative treatment of the reactivity of conjugated molecules, there are roughly two groups of methods according to the models assumed for the process of chemical change. The first, which may be referred to as the "static method," is based on the hypothesis that the entire process of chemical change is governed by the static interaction between the reacting molecules and the attacking species in the initial stage of reaction. Thus, for example, the core position of higher π -electron density in a conjugated molecule is more amenable to electrophilic attack, as assumed in Wheland & Pauling's pioneering work (90) on the orienting effect of substituents in benzene. The view was extended into a more general form by Coulson & Longuet-Higgins (91), who amplified the role of polarizability of the carbon atom to be attacked. The extension revealed the practical importance of the polarizability for interpreting different ionic reactivities of various positions in an alternant hydrocarbon which has a uniform distribution of π -electronic charge within the limitation of the simple Hückel theory. In radical reactions neither the π -electron density nor the polarizability can be a reactivity index; instead, the free valence (92) serves to fill in the defects of the static method.

The second method, which may be called the "dynamic method," is related to the calculation of the relative stability of the hypothetical transition complexes. This latter method is preferable to the static method because it is capable of explaining, from a unified viewpoint, the reactivities of different positions, not merely in one conjugated molecule but also in various conjugated molecules, toward any of the three attacking species (electrophilic, nucleophilic, and radical).

The dynamic method is seemingly divided into two subgroups. One of these is the so-called "localization method" originated by Wheland (93), in which the π -orbital of the attacked core atom is removed or "localized" from the conjugation in the hypothetical transition state, and the decrease in unsaturation energy is assumed to be parallel to the true activation energy. Because the residual π -systems formed by putting an atomic orbital out of conjugation are generally of lower symmetry than the molecules under question, the energy calculation involved in Wheland's localization theory is usually complicated. The calculation would be quite cumbersome if one wanted to compare, for instance, the localization energies of the 18 different positions

of 1,2-benzanthracene. This formidable difficulty inherent in the localization method was greatly reduced by Dewar (94), who ingeniously utilized the nature of the nonbonding molecular orbitals of the resultant π -systems in a perturbation approximation of the localization energies of the parent alternant hydrocarbons. Another approximation procedure has recently been proposed by Koutecký (95). The interrelations among free-valence, polarizability, Wheland's localization energy, and Dewars' approximate localization energy were theoretically investigated by Dewar (96), Baba (97, 98), and Fukui, Yonezawa & Nagata (99). Thus, in the cases of alternant hydrocarbons, it seems unnecessary to compare the relative merits of these four theoretical quantities except for the difference in labor required for computation. For non-alternant molecules, however, there still remains a question as to which is more important for predicting the most reactive positions, the π -electron density or the localization energy (99, 100).

Both static and localization methods have been widely used to interpret the experimentally observed chemical behaviors of various conjugated molecules in addition reactions and in substitution reactions. Many such examples have been given (3, 11, 100, 101). Two papers should be mentioned as examples of current investigations along this line. One is on electrophilic and radical additions of monoolefins by Sato & Cvetanović (102), while the other is on deuterium substitution reaction of dimethylnaphthalenes by Dallinga, Smit & Mackor (103). Fukui, Kato & Yonezawa (104) applied the localization method uniquely to the bimolecular nucleophilic substitution of saturated aliphatic halides, $A^- + RX \rightarrow AR + X^-$, where A^- , R, and X respectively signify nucleophilic reagent, alkyl group, and halogen atom. In this treatment, a mobile σ -electron model (105) was assumed for the saturated molecular skeletons and the localization energy was defined in a manner analogous to that of Wheland (93) for aromatic substitution.

The other category of the "dynamic method" emphasizes that the "delocalization" of π -orbitals on attacking reagents and reacting molecules in hypothetical transition complexes contributes directly to lowering the actual activation energies. This view certainly seems to be the current way of looking at the reactivities of conjugated molecules in general. The theories of reactivities of conjugated molecules, developed on the basis of the above delocalized transition-state model, include the "frontier electron theory" by Fukui *et al.* (99; 106 to 113) and the "charge-transfer theory" by Brown (114, 115), both of which will be described in some detail below.

Delocalization theory.—The "frontier electron theory" originally was aimed at predicting the most reactive core positions of alternant hydrocarbons in electrophilic substitutions (106). The theory was then based on a rather intuitive, and yet reasonable, idea that the least tightly bound electrons in a molecule would play a decisive role in electrophilic substitutions. Thus, for many alternant hydrocarbons it was shown that the electrophilic substitutions actually take place at the positions of the highest density of electrons in the highest occupied molecular orbital of the ground state. The

pair of electrons in this particular orbital were then termed the "frontier electrons" for electrophilic reactions. This theory was further applied to electrophilic, nucleophilic, and radical substitutions of heteroaromatics, including non-alternants, by specifying the frontier electrons according to the type of reaction as follows (107): (a) In the case of electrophilic reactions, the frontier electrons are those two electrons in the highest occupied molecular orbital in the ground state. (b) In the case of nucleophilic reactions, the frontier electrons are the two dummy electrons assumed to occupy the lowest unoccupied molecular orbital in the ground state. (c) In the case of radical reactions, the frontier electrons include one of the two electrons in the highest occupied molecular orbital and the dummy electron assumed to occupy the lowest unoccupied molecular orbital in the ground state. For alternant hydrocarbons, these specified pairs of frontier electrons have identical distribution because of the symmetric nature of the molecular orbitals in the simple Hückel theory (91). In the cases of odd π -electron systems and biradical states, the frontier electrons are specified correspondingly according to the principle stated above.

Fukui, Yonezawa & Nagata (108) gave an adequate justification for the frontier electron theory, adopting as a model for the transition state in a substitution reaction the structure presented by Pickett, Muller & Mulliken (116) to explain the stabilization of $C_6H_7^+$ ion. In the transition-state model the aromatic π -orbitals are assumed to be conjugated with a pseudo- π -orbital made from the orbital on the displacing atom and the orbital on the atom being displaced. The energy of the whole system is divided into σ - and π -parts. The σ -part of the energy has a maximum in this transition state, and the increase in the σ -energy accompanying the process leading to the transition state is constant over all molecules subjected to a similar type of substitution. Then the hyperconjugation between the aromatic π -orbitals and the pseudo- π -orbital contributes to stabilizing the transition complex.

By regarding as small the resonance integral γ , between the pseudo- π -orbital h and the π -orbital of the core atom r to be attacked, Fukui *et al.* (108) applied the perturbation theory and expressed the stabilization energy due to the hyperconjugation as

$$E_s = -H_r\gamma^2/\beta, \quad 5.$$

where β is the resonance integral for a carbon—carbon π -bond in conjugated molecules, and H_r is the "generalized superdelocalizability" (the measure of the hyperconjugation between the pseudo- π -orbital and the aromatic system through the core carbon r).

$$H_r = \sum_j [(\nu_j - \nu)(C_{jr})^2\beta/(\epsilon_j - \alpha_h)] \quad 6.$$

Here ν_j and C_{jr} respectively denote the number of π -electrons (0, 1, or 2) and the LCAO coefficient for the π -orbital of the atom r in the j^{th} molecular orbital of the isolated molecule; ϵ_j is the energy of the j^{th} molecular orbital; α_h is the Coulomb integral of the pseudo- π -orbital; ν is an integer taken as 0,

1, or 2 accordingly as the replacing reagent is electrophilic, radical, or nucleophilic; and the summation extends over all molecular orbitals. If one can safely assume that α_h is very close to the Coulomb integral α of a carbon atom in conjugated molecules (the quantity H_r , when $\alpha_h = \alpha$, being called the "superdelocalizability" and denoted by another symbol S_r), then it is seen from Equation 6 that the superdelocalizability S_r is determined predomi-

TABLE I
THEORETICAL REACTIVITY INDICES AND METHYL AFFINITIES
OF EVEN-ALTERNANT HYDROCARBONS

Hydrocarbon	Most reactive position,* r	Reactivity indices†				Methyl affinity‡
		S_r	f_r	L_r	L_r'	
Naphthacene	5	1.5049	0.530	—	1.13	9250
Anthracene	9	1.3137	0.520	2.01	1.26	820
1,2-Benzanthracene	10	1.2502	0.514	—	1.35	468
1,2,5,6-Dibenzanthracene	9	1.1460	0.498	—	1.51	—
Stilbene	7(a)	1.1380	0.481	2.16	—	183
Pyrene	8	1.1150	0.469	2.19	1.51	125
Chrysene	2	1.0442	0.457	—	1.67	58
Phenanthrene	9	0.9975	0.451	2.30	1.79	27
Naphthalene	1	0.9944	0.452	2.30	1.81	22
Biphenyl	2(o)	0.9770	0.436	2.38	2.07	5
Benzene	—	0.8333	0.398	2.54	2.31	1

* All of the four indices predict the same position for each hydrocarbon. As to the numbering, see literature (3).

† S_r , superdelocalizability (112); f_r , free valence (3); L_r , localization energy in units of $-\beta$ (101); L_r' , approximate localization energy in units of $-\beta$ (94). Each hydrocarbon has the same value of S_r , L_r , or L_r' for electrophilic, nucleophilic, and radical reactions.

‡ Szwarc, M., *J. Polymer Sci.*, **16**, 367 (1955)

nantly by the term whose j is m (the highest occupied orbital) or $m+1$ (the lowest unoccupied orbital) and that S_r is greatest when r is the position of the largest $(C_m)^2$ or $(C_{m+1})^2$. That is, the main part of the stabilization of the transition state brought about by the hyperconjugation is attributable to the frontier electrons. The frontier electron theory was thus justified.

The superdelocalizability may be employed as an index for additions as well as for substitutions. For comparison's sake, the superdelocalizability (S_r), the free valence (f_r), and the localization energies (L_r and L_r') for the most reactive positions of various hydrocarbons are summarized in Table I, along with the experimental data of their affinity toward the methyl radical. Since the correlations of S_r with f_r , L_r , and L_r' for alternant hydrocarbons have been proved mathematically by Fukui *et al.* (99), it is now meaningless

to compare the reliability of these four indices for alternant π -systems. However, it is significant to decide which of these indices corresponds most closely to the true mechanism of reactions. This could probably be done by accumulating both theoretical and experimental data for many reactions of hetero-conjugated and non-alternant molecules.

The difference in physical significance of the transition-state models inherent in the indices is perhaps more remarkable for additions than for substitutions. For instance, it was shown by Sato & Cvetanović (102) that the localization energies of monoolefins, calculated by inclusion of the hyperconjugation effects of methyl and methylenic groups within the molecules, have no general correlation with the rates of radical addition toward these hydrocarbons. The failure in the correlation is understandable because Wheland's idealized transition-state model for substitutions, in which the π -orbital of the reaction center is assumed completely localized, is too far from the true transition state for additions; the model is identical even with the structure of the final addition products.

In view of these circumstances, it was rather natural for Yonezawa *et al.* to have applied the concept of hyperconjugation to the transition states of radical (109, 110) and ionic (111) polymerizations of vinyl monomers. The propagation process of vinyl polymerizations is merely the repetition of addition reactions between monomer molecules and polymer radicals (or ions). The transition state for addition reactions was defined (109, 110) to be such that all the π -electrons are delocalized over the entire π -system lying with a set of atomic π -orbitals perpendicular to a single plane. The stabilization energy of the transition state due to the hyperconjugation accounted for the relative rates of the propagation steps of many monomer-polymer systems satisfactorily (109, 110, 111), and the positions of preferential attack in both monomers and polymers were predicted from the distribution of the frontier electrons in good accord with experiment (110, 111). On the other hand, it was demonstrated by Yonezawa *et al.* (111, 117) and by Fueno, Tsuruta & Furukawa (118, 119) that the localization energies can also be used as a reactivity index for monomers and polymer radicals. Thus, the adequacy of interpreting the propagation rates in terms of the resonance stabilization alone was questioned [Fueno, Tsuruta & Furukawa (118)].

Fukui, Yonezawa & Nagata (112) further investigated the mechanism of aromatic substitutions, paying particular attention to the process of charge transfer between the attacking species and the aromatics during the course of reaction. The principle of the approach was as follows: Since the π -electron density on the pseudo- π -orbital in their transition-state model is related to the amount of charge transfer through the hyperconjugation between the pseudo- π -orbital and the aromatic nucleus and varies as the reaction proceeds, the course of the reaction can be followed by the change of this π -electron density. Specifically, the π -electron density q_h on the pseudoatom was expressed in terms of the Coulomb integral $\alpha + h\beta$ of the pseudoatom, and the resonance integral γ between the pseudoatom and the carbon atom

to be attacked. The h was varied according to the change of q_h , in a fashion similar to the ω -technique described already, until the self-consistency between h and q_h was established for a given γ . Thus the proceeding of the charge transfer was persued dynamically with a gradual increase of γ . The technique was exemplified for electrophilic, radical, and nucleophilic substitution of benzene. Of course, the value of γ can not be increased infinitely. It is thus necessary to determine the limiting value of γ corresponding to the transition state. When this is done the final value of h is also fixed correspondingly. Fukui, Yonezawa & Nagata (112) stated that, in principle, such limiting values as γ_i and h_i could be determined by an elaboration making the total energy (including that of the σ -part) maximum, or by a superposition of a similar γ - h - q_h relation for the reverse reaction. For simplicity, however, they treated the problem by assuming both γ_i and h_i to be known constants depending on the reagent and the type of reaction.

The semi-quantitative conclusions derived from the above theoretical investigation were as follows. (a) An electrophilic substitution can take place only when the energy of the lowest unoccupied orbital of the isolated electrophilic reagent is lower than that of the highest occupied orbital of the substrate molecule; and a nucleophilic substitution can occur only when the highest occupied orbital of the isolated nucleophilic reagent lies above the lowest unoccupied level of the substrate molecule [in accordance with the empirical generalization presented by Nagakura & Tanaka (120, 121, 122)]. (b) There are no special restrictions as to the energy of the half-occupied orbital of a radical reagent in radical substitution. (c) The energy of the pseudo- π -orbital in an electrophilic (or a nucleophilic) substitution rises (or falls) to the height of the highest occupied orbital (or the lowest unoccupied orbital) of the isolated substrate molecule instantaneously with hyperconjugation, and then it increases or decreases continuously with increasing extent of hyperconjugation until it reaches a limiting value in the transition state, where the value is not far from the Coulomb integral of a carbon atom. In the above conclusions the discriminating property of frontier orbitals are clearly recognized.

The hyperconjugation treatment, which is the physical basis of the frontier electron theory, utilizes a perturbation method for describing the progress of the interaction between conjugated molecules and attacking reagents. In this connection, Fukui *et al.* (123, 124) presented the method of the perturbed secular determinant, from which many useful equations were derived for orbital energy, electron density, and bond order of conjugated systems when perturbed by either changes of integral parameters or bonding to other conjugated systems or by both of these.

The prominent role of charge transfer in stabilizing the transition states is visualized in the Fueno, Ree & Eyring work (125) on the antioxidizing reaction of phenolic compounds. It was assumed there that the primary interaction between phenols and chain-carrier radicals in autoxidation systems would take place through the phenolic oxygens. Then the reactivities

toward radicals of several phenols, including poly-functional phenols, were found to be closely related to both the resonance stabilization and the degree of charge transfer calculated for a transition state of the reactions, whereas the π -electron density and free valence for the oxygen atoms in separated phenols had no correlation with their radical reactivities.

On the basis of several lines of evidence, Brown (114) has proposed a new mechanism of aromatic substitutions. The mechanism involves the formation of stable unsymmetrical charge-transfer complexes between reagents and aromatic molecules. The stabilization energy of the aromatic molecules caused by the complex formation is then assumed to be the most important factor affecting their reactivity. In treating this charge-transfer stabilization, Brown (114, 115) made use of the simple configuration-interaction method adopted by Mulliken (126) for the discussion of charge-transfer complexes. Thus, in an electrophilic substitution, the stable charge-transfer complex was considered as an intermediate between the configuration without the charge transfer and the configurations corresponding to the transfer of one electron from occupied orbitals ϕ_j 's of the aromatic molecule to the lowest unoccupied orbital ϕ_h of the electrophilic reagent. It was then proved that the stabilization energy (in units of $-\beta$) is given by the largest root (Z_0) of the equation:

$$Z - \sum_j \frac{c_j}{Z - Y_j} [2g^2(C_{jr})^2 / (Z - Y_j)] = 0 \quad 7.$$

where C_{jr} is the LCAO coefficient of the r^{th} atomic orbital in ϕ_j , g is a dimensionless positive quantity defined as the ratio of the resonance integral between the r^{th} atomic orbital and the electrophile orbital in the transition state to β (i.e., $g = \gamma/\beta$), and Y_j is the energy difference (in units of $-\beta$) between the ϕ_j whose energy is $\epsilon_j (= \alpha + \lambda_j\beta)$ and the ϕ_h whose energy is $\epsilon_h (= \alpha + h\beta)$. Since $Y_j = h - \lambda_j$, the Y_j is negative or positive as the level of the ϵ_h is above or below that of the ϕ_j , respectively. It is apparent that the major contribution to the Z_0 comes from the highest occupied orbital (i.e., the frontier orbital) of the molecule, the orbital energy being $\epsilon_f (= \alpha + \lambda_f\beta)$. Then,

$$Z_0 = [Y_f + \{Y_f^2 + 2g^2(C_{fr})^2\}^{1/2}] / 2 \quad 8.$$

Following Nagakura & Tanaka's generalization concerning the energy levels of the reactants (120, 121, 122), Brown considered that Y_f should be positive in the case of electrophilic substitutions. He then demonstrated that the rate of nitration of a large variety of conjugated hydrocarbons at various core positions runs closely parallel to the Z_0 -value calculated from Equation 8 by adjusting the two parameters g (< 1) and h ($> \lambda_f$).

It is of interest to compare Brown's charge-transfer theory with the frontier electron theory of Fukui and co-workers. Both theories have apparent similarity in that the major contribution to either index comes from the frontier orbital and that the intramolecular orientation in substitutions is attributable to the frontier electron distribution. They have, however, an

intrinsic difference in formalism. This becomes obvious when Equation 8 is expanded with respect to g ; thus,

$$Z_0 \simeq \begin{cases} Y_f + 2g^2(C_f)^2/Y_f & \text{when } Y_f > 0 \\ 2g^2(C_f)^2/(-Y_f) & \text{when } Y_f < 0 \end{cases} \quad \begin{matrix} 9a. \\ 9b. \end{matrix}$$

Equation 9a is an approximation of Brown's general Z_0 -value, and Equation 9b is nothing but g^2 times the one-term approximation of the generalized superdelocalizability (Eq. 6) by Fukui *et al.* (112). Fukui and co-workers (127) showed by a more general expansion procedure that Equations 9a and 6 can both be derived directly from Equation 7 according as Y_f is positive and negative, respectively. The difference in formalism between these two indices, then, would seem to have arisen simply from the different assumptions concerning the relative height of the energy level for the reagent in "charge-transfer complexes." Actually, however, Brown's charge-transfer complex theory (114, 115) and Fukui, Yonezawa & Nagata's hyperconjugation theory (112) are basically different in treating the mechanism. In the former the formation of charge-transfer complexes has been assumed rate-determining and the transition state of this step has not been defined clearly, whereas in the latter the reaction rate has been related to the delocalization stability of the transition state, which was reasonably defined. Comparative discussions of these two theories have been made by Brown (114, 115) and by Fukui and his co-workers (127).

In unimolecular nucleophilic substitutions of aliphatic halides the rate-determining step is the ionic dissociation: $RX \rightarrow R^+ + X^-$, where R and X are an alkyl group and a halogen atom, respectively, and the dissociation is promoted by solvents. Substitution reactions are completed by an instantaneous addition of the nucleophilic reagent A^- to the alkyl cation R^+ . The overall rate of this type of substitution is related to the polarity of the dissociating C—X bond [Fukui, Kato & Yonezawa (104)] or to the stability of the R^+ ion [Streitwieser (128)]. Adopting the latter criterion, Ron, Halevi & Pauncz (129) investigated the effect of deuteration in the methyl group on the rate of solvolysis of $CH_3 \cdot CH_2X$. On deuteration, the hyperconjugative stability of $CH_3 \cdot CH_2^+$ ion is affected by the changes in electronegativity of the H_3 pseudoatom and in overlap of the $C \equiv H_3$ pseudo- π -bond. Qualitatively, the configurational change of the CH_3 group upon deuteration is such that the C—D bond length is shorter than that of the C—H bond, and the bond angle θ_{DCD} is larger than θ_{HCH} . As a result, in the $C \equiv D_3$ group the Coulomb integral for the pseudoatom should be less negative (i.e., the pseudoatom being more electropositive), and the overlap and resonance integrals for the pseudo- π -bond are obviously larger than in the $C \equiv H_3$ group. Ron, Halevi & Pauncz (129) thus computed, using the iterative " ω -technique," the changes of the hyperconjugative stability and π -electron distribution in the ethyl carbonium ion when deuterated. The results were: (a) that the increased effective electropositivity of the D_3 pseudoatom and the increased $C \equiv D_3$ overlap oppositely affect the delocalization stability,

the combined effect being in favor of the hyperconjugative destabilization of the CD_3CH_2^+ relative to $\text{CH}_3\cdot\text{CH}_2^+$ in agreement with observation; and (b) that more positive charge is delocalized to the methyl group in CD_3CH_2^+ than in CH_3CH_2^+ . Although the two results sound inconsistent in the sense of chemical intuition, this superficial inconsistency is rather a natural consequence of the fact that the electron distribution in molecules is considerably more sensitive to the variation in the electronegativity of the atoms involved than to the variation in the overlap of atomic orbitals. Therefore, it seems of great importance to bear in mind that the "hyperconjugative stabilization" and "hyperconjugative electron-transfer" are not necessarily synonymous in any delocalization theory.

From what has been reviewed above, it is seen that the reactivities of conjugated molecules customarily have been discussed within the scope of the simple Hückel method, where the electronic interaction term of the Hamiltonian is suppressed into an average core potential. In this oversimplified approximation, the total π -electron density is unity for all positions of alternant hydrocarbons. When one makes use of the self-consistent field method, where electronic repulsions are adequately incorporated, then the uniform distribution of the total π -electron density is removed. Then it is obvious that, whatever the approximation may be, the total π -electron density can never explain how both the electrophilic and nucleophilic reactions of a given alternant hydrocarbon take place at a particular position. A question now arises: How reliable will the reactivity indices be when electronic repulsions are taken into account? The total π -electron density is out of the question, of course, at least in the case of alternant hydrocarbons. Fukui, Morokuma & Yonezawa (130) demonstrated that the frontier electron density is still a useful index in SCF-treatments for checking the orientation in butadiene, naphthalene, and anthracene but that free valence varies very easily and, in cases, leads to inconsistent results depending on the degree of approximation. Using an SCF-like procedure proposed by Pople (9), Fukui, Morokuma & Yonezawa (131) calculated localization energies of several hydrocarbons in ionic and radical reactions and observed that the energies thus obtained are also satisfactory measures for reactivity.

Applications to biochemistry.—Biochemical phenomena have received continuous attention. Pullman and his collaborators have discussed the mechanism of the metabolic breakdown of hemoglobin (132) and the biochemical activity of porphyrin complexes (133) in terms of the oxido-reductive properties of these compounds deduced from the quantum-mechanical treatments. By focusing attention on the stability of "dispositive bonds" in various biochemical substances, including the so-called energy-rich phosphoric esters, Pullman & Pullman (134) revealed a fairly systematic understanding of the general feature of the mechanisms of enzymatic hydrolyses. Some aspects concerning the electron-donor or electron-acceptor abilities of biochemical compounds and the antitumor activities of certain cancer-chemotherapeutic agents have been presented by Pullman & Pullman (135).

Fukui and his co-workers have furnished the tests of the frontier electron theory in understanding the biochemical activities of several groups of conjugated compounds [the auxin activity of benzoic acid derivatives (136); the nicotine-like stimulant activity of phenyl ether choline (137); the energy-rich bonds in phosphates (138); the antifungal activity of quinoline- and pyridine-N-oxides (139); and the carcinogenic activity of aromatic hydrocarbons (140), heteroaromatic compounds (141) and nitroquinoline-N-oxides (142)]. The results obtained are encouraging in most cases and shed some illumination on the nature of the above biological substances as well as on the mechanism of their biochemical reactions.

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THERMOCHEMISTRY AND THERMODYNAMIC PROPERTIES OF SUBSTANCES^{1,2}

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INTRODUCTION

As the number of papers on the thermochemical and thermodynamic properties of substances continues to grow, the majority of the authors in reviewing this area have resorted to a tabular presentation of the annual output of research data in the form of a substance-property index with an accompanying exhaustive bibliography. Such a space economy measure served as a temporary solution. With increased activity in this area of physical chemistry, it appears that other procedures need to be developed to make this invaluable substance-property index and references available to all workers through some publication other than the Annual Review volume. In this manner, critically needed textual space will again become available to authors for a more thorough discussion of trends and developments in thermochemistry and chemical thermodynamics. It is hoped that this current review, featuring such tabular summaries of data, will be the last one to have such tables included. In spite of the large number of references included in this review, the need for even larger quantities of reliable thermodynamic data is now greater than ever. Accepting the recent estimate of the *Chemical Abstracts* that 50,000 new compounds are being identified and prepared each year and recalling that in our backlog of unstudied or thermodynamically uncharacterized substances there are at least a million or more compounds, the need for accelerated and coordinated programs of thermochemical, thermodynamic, and related spectroscopic studies is truly very great.

The several topics covered are discussed in the following order: foundations of thermodynamics, special topics which include fundamental constants, temperature, selected or "best" values of thermodynamic data, reviews and correlations, thermodynamic properties from spectroscopic investigations, apparatus and techniques, and finally, the description of the substance-property index and the three tables. Topics covered by other chapters in this volume or in recent volumes involving thermodynamic properties have been deleted: specifically, high temperature ($T > 1500^\circ\text{K.}$) and high pressure studies ($p > 1 \times 10^4 \text{ atm.}$), surface phenomena (an exception are calorimetric heats of adsorption included in Table III), mixtures, solutions, alloys, electrode processes, magnetic phenomena, and irreversible thermodynamics.

¹ The survey of literature pertaining to this review was concluded December 15, 1960.

² This work was performed under the American Petroleum Institute Research Project 44 and the Manufacturing Chemists' Association Research Project, now located at A & M College of Texas, College Station, Texas.

FOUNDATIONS OF MACROSCOPIC THERMODYNAMICS

Many of us tend to overemphasize the elegance and completeness of the classical formulation of macroscopic thermodynamics. Recent activities and accomplishments in the area that deal with new formulations of macroscopic thermodynamics, other than the microscopic general kinetic theory or statistical formulations, demand a hearing to see how the axiomatic and geometric formulations of the basic thermodynamic principles may provide new insight into both old and new thermodynamic phenomena.

In any axiomatic approach to the foundations of thermodynamics, the basic assumption is made that equilibrium states exist and can be defined for any physical or material system by a finite set of macroscopic thermodynamic variables. This assumption stipulates that all those parts of physics and chemistry outside of thermodynamics are known and provide the kind of macroscopic information for complete thermodynamic characterization of a chosen physical system under any existing set of conditions. The universal applicability of this powerful tool of science continually awes the mature research man, frustrates the apprentice, and challenges new generations to examine more closely its mathematical structure and logical foundations. In the twilight of his years, while reminiscing on his early training and interests, Einstein (1) remarked: "A theory is the more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended is its area of applicability. Therefore, the deep impression which classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown."

Once any theory has reached a certain stage of maturity, it is vulnerable to a closer scrutiny of its basic assumptions and definitions, as based on empirical observations, to determine whether a more logically coherent group of axioms can be selected from which all theorems can be obtained by deductive reasoning. The first such attempt was made by the mathematician, Carathéodory in 1909 at the suggestion of his physicist colleague, Max Born. Except for the well known writings of Born, little had been added to the literature until Landsberg's comprehensive article appeared in 1956 (2). Not only was he successful in removing certain deficiencies in the axiomatic approach of Carathéodory but by considering the thermodynamic space as being *bounded*, i.e. boundary points need to be included, he successfully deduced the Third Law or the Unattainability Principle from the Second Law, which has challenged workers like Nernst, Einstein, Lewis, and Simon for many years. In a recent article (3), Landsberg shows how the concept of negative temperature finds a natural place in Carathéodory's approach to classical thermodynamics. In a footnote to this article, Landsberg announces that a detailed exposition of Carathéodory's method is contained in his forthcoming book on thermodynamics. It is hoped that Landsberg will introduce the average worker in thermodynamics to the necessary concepts and tools of set theory and elementary topology needed in a full exposition. A more ele-

mentary but complete treatment of Carathéodory's approach to the first two laws of thermodynamics may be found in Wilson's recent text (4).

Recently Falk & Jung (5) criticized Carathéodory's deductive axiomatic procedure and presented a new, more general axiomatic construction of thermodynamics. In any axiomatic treatment of a theory or discipline of physics, there are two possible procedures. The deductive method starts with the most general principle possible, such as Hamilton's principle in mechanics and derives from it particular consequences that are experimentally demonstrable. Such a procedure was essentially used by Carathéodory with his Principle of Inaccessibility which states "that in every neighborhood of an arbitrary state, there are states adiabatically inaccessible." In his deductive method, Carathéodory essentially follows the classical construction of thermodynamics by using, in his rigorous formulation, the concept of heat defined through linear Pfaffian differential equations, thus limiting himself to thermal systems, i.e. systems with a temperature, which is in general an unnecessary limitation. The second possible axiomatic procedure is the constructive method. This constructive axiomatic method uses a system of axioms whose physical content is directly accessible through experiment. On these principles or axioms the theoretical framework, which can culminate in certain general fundamental laws, is constructed. Such a procedure is followed by Falk & Jung. An informative report by Falk on this new axiomatic treatment of thermodynamics, which lacks some of the details of proof as given in the original article, is now available (6). As a result of this treatment, Falk (7) derives a new formulation of the Third Law applicable to all physical systems (including thermal ones, e.g., Nernst heat theorem) which he states as follows: "*Third Law*.—Energy as well as entropy of any physical system each has a smallest value which can be normalized to zero. When the energy assumes its smallest value so does the entropy, but the reverse need not be true."

Among the usual quota of new pedagogical and technical books in this area, two rather unusual books have appeared during the past year. Callen (8) has written an elegant introductory text on thermodynamics based on a modified postulatory approach, as developed by Tisza which features states rather than processes as fundamental constructs. Another unusual text was introduced by Tribus (9) based on Jaynes' earlier work on information theory and statistical mechanics. Tribus derives all the relations of macroscopic thermodynamics starting with the basic and primitive ideas of information theory and its mathematical formalism. In concluding this section, it is appropriate to mention Koenig's recent study of a detailed history of the Second Law of thermodynamics (10).

SPECIAL TOPICS

FUNDAMENTAL CONSTANTS AND TEMPERATURE

The problem of new fundamental constants in physical chemistry has still not been completely settled as of the end of 1960. DuMond, in an extensive

article (11), reviews the status of our current knowledge of the fundamental constants of physics and chemistry in terms of work performed or in process since 1955. Rossini presented a paper on the present state of knowledge on the fundamental constants of physical chemistry at the *IUPAC 1959 Chemical Thermodynamics Symposium* held in Austria as noted by Waddington (12) in his excellent review of this symposium. The new set of fundamental and auxiliary constants for physical chemistry will need to take cognizance of (a) the absolute temperature of the triple point of water, 273.160°K. (exactly), (b) small improvements in the velocity of light, Planck's constant, and the Faraday constant, and (c) the common scale of atomic weights for chemists and physicists defined by taking 12 (exactly) grams of isotopically pure carbon-12 as one mole. The carbon-12 atomic weight scale was approved by *IUPAC* in August, 1959 and awaits similar action by *IUPAP*. Once approved, this new carbon-12 scale will decrease the present "chemical" atomic weights by 43 parts per million and increase the present "physical" atomic weights by 318 parts per million. Such a change will give common values of the Faraday, Avogadro, and gas constants for both chemists and physicists. Attention is called to the revised *IUPAC Manual on Physico-chemical Symbols and Terminology* by Christiansen published in the *Journal of the American Chemical Society* (13). With respect to new symbols, Giauque (14) made an interesting suggestion for a common unit to apply to the useful thermodynamic quantities such as F/T , H/T , S , and C_p , namely, 1 gibbs (gbs) = 1 defined cal. (°K.)⁻¹.

Brickwedde (15) reported on a conference held in Leiden, Netherlands in 1959 regarding the temperature scale, 10°K. to 90°K. It was agreed to make the platinum scale between 20°K. and 90°K. continuous with the *International Temperature Scale* above 90°K. Accordingly, 90.18°K. (-182.97°C.), the normal boiling point of oxygen on the *International Temperature Scale*, was adopted for the oxygen calibration point, and for the hydrogen fixed point, a value of 20.26°K. was assigned to the temperature of the normal boiling point of the 20°K. equilibrium mixture of *o*- and *p*-H₂. An important paper on the "1958 ⁴He Vapor Pressure Scale of Temperature" appeared this year (16). This paper reviews the history and recommendations leading to the adoption of this scale as an international standard for thermometry from 1° to 5.2°K. and presents the necessary tables (van Dijk, Durieux, Clement, Logan) for its practical use. The 1958 ⁴He temperature scale is reproduced in the data catalog of the Manufacturing Chemists' Association Research Project to an accuracy of ±0.000°C. in terms of appropriate sets of Antoine vapor pressure constants (17). The *Proceedings of the International Committee on Weights and Measures*, which include additional reports dealing with temperature measurements and temperature scales, is now available (18).

SELECTED OR BEST VALUES OF CHEMICAL THERMODYNAMIC DATA

Two important aspects of the problem concerning more rapid progress in chemical thermodynamics are the availability of compounds of defined

or certified purity, and the matter dealing with the evaluation and correlation of physico-chemical data leading to critically selected values for various chemical substances. Two timely conferences held during the past two years dealt with these matters. A *Conference on Chemical Compounds of Certified High Purity* sponsored by the National Science Foundation and the National Academy of Sciences-National Research Council was held in Washington, D. C. in June, 1959 (19). Recommendations resulting from this conference included the founding of a permanent information center for pure substances and the establishment of a permanent technical organization with responsibility for the identification, preparation, purification, and certification of chemical compounds of high purity. *Information Processing for Critical Tables of Scientific Data* was the title of a new Gordon Conference held in June, 1960 and sponsored by the NAS-NRC Office of Critical Tables. The purpose of this conference was to bring together active workers in the field of documentation of numerical data of the physical sciences and to discuss the problems associated with the evaluation, processing, compilation, and publication of numerical data. The introductory paper by Bridgman, dealing with some of the principles involved in selecting a "best" value or estimating how good the "best" value may be, is now available (20). The third number of the OCT (Office of Critical Tables) *Newsletter* has been distributed (21). To keep workers in the various disciplines informed on progress in the general area of critical data compilations, it is hoped that this letter can receive even wider distribution in the future.

In the area of compilations of selected thermodynamic data, a new issue of data sheets on *Thermodynamic Properties of Metals and Alloys* appeared, under the continuing direction of Hultgren (22). Of particular interest to this review is the complete thermodynamic data for the following elements: Zn, Cd, Cu, Ag, Au, Pt, Ta, Dy, Gd, Eu, Sm, Nd, Be, Mg, Ca. The S_{sat} and $H_{\text{sat}}-H_0$ values for most of these elements agree with those given by Stull & Sinke (23). In the *Contributions to the Data on Theoretical Metallurgy Series*, Kelley's Bulletin 584 of the Bureau of Mines (24) appeared giving $H_T-H_{298.15}$ and $S_T-S_{298.15}$ values for some 90 elements and 800 compounds of these elements in both tabular and algebraic form including heat capacity data. The present work is a revision and extension of Bulletin 476 and includes data available to September, 1958. A convenient and precise algebraic procedure that avoids numerical integration was devised by Kelley for the calculation of entropy increments above 298.15°K. In the year ending June 30, 1960, the American Petroleum Institute Research Project 44 issued 261 loose-leaf data sheets on *Selected Values of Hydrocarbons and Related Compounds* (25). Attention is drawn to the new "m" tables on temperature, heat, and entropy of transitions, the P-V-T and related thermodynamic data for *n*-butane and *n*-pentane, and the revised and new "n" tables for standard heats of combustion. The "n" tables are based on the recent heat of combustion work of Rossini and his associates (26 to 31). The Manufacturing Chemists Association Research Project has recently published (17) extensive vapor pressure

data, based on the Antoine vapor pressure equation, of elements and their compounds with standard order numbers below carbon (No. 23), i.e. elements and all existing compounds of these elements in Groups V-A, VI-A, VII-A, and the inert gases. From the given Antoine constants, heats and entropies of vaporization can be readily calculated.

REVIEWS AND CORRELATIONS

Reviews of chemical thermodynamic data on classes of substances that include a critical evaluation of the existing experimental data are always welcomed. To be noted among these are reviews by Westrum (32) and Evans *et al.* (33) on boron and boron compounds, Mah's (34) work on manganese and its compounds, and the thorough review of the properties of nitric acid by Stern *et al.* (35).

Sound correlation procedures, when applied to chemically related groups of compounds, will create thermodynamic functions for compounds with as high a degree of accuracy as the measured values. The incremental procedure, combined with statistical techniques, was utilized by McCullough's thermodynamic group at Bartlesville (36) to prepare tables of ideal gas thermodynamic functions, from 0° to 1000°K., for 100 straight chain alkane thiols, sulfides, and symmetrical disulfides. For the calculation of the ΔH_f° and ΔF_f° values, Good *et al.* (37) redetermined the heat of formation of aqueous sulfuric acid to a higher degree of accuracy than was previously available. Significant corresponding state correlations for liquids and gases are given by Everett (38), Bondi (39), Kurata (40), Thodos (41), and Bloomer & Peck (42). As an aid in the evaluation and correlation of data, Margrave (43) proposes a convenient graphical procedure for determining standard equilibrium data at 298.15°K. from measurements made above room temperature. Edmister's extensive series of papers (44, 45), on the application of thermodynamics to the hydrocarbon field is being continued. Maslov has extended his semi-empirical procedures for correlating and calculating heats and free energies of formation for a variety of inorganic substances (46 to 52). To encourage and promote the inclusion, in scientific papers, of the primary data from calorimetric and thermodynamic studies, the 15th *Calorimetry Conference* held at Gatlinburg, Tennessee in September, 1960 adopted a revised and expanded resolution (53) outlining the minimum publication standards for the guidance of authors, editors, and referees of calorimetric and thermodynamic papers. A similar resolution is needed in the area of precise measurement of physical properties of importance in thermodynamic calculations.

THERMODYNAMIC PROPERTIES FROM SPECTROSCOPIC INVESTIGATIONS

The usual yearly number of publications from authors engaged in spectroscopic work, who report thermodynamic functions calculated by the accepted statistical mechanical procedures from spectroscopic information, are included in this review. All of these publications are cited under tabulated sub-

stances for which the properties "*rstv*" are reported. The consistency with which investigators like Cleveland and co-workers (54 to 61) report thermodynamic functions in every applicable spectroscopic paper is noteworthy. United States authors have become more helpful in these matters.

The improvement of spectroscopic instrumentation by the leading instrument makers, individual investigators, and spectroscopic laboratories continues at a steady pace. Of special importance, for increasing the utility of the spectroscopic method for the determination of thermodynamic functions, are the infrared grating instruments of higher resolution, the increased activity in connection with far infrared investigations (30 to 500 plus microns), and the availability of good photoelectric Raman spectrophotometers like the Cary Model 81 Raman Spectrophotometer. The status of far infrared investigations has been summarized recently by Palik in a bibliography (62). The accurate measurement or determination of frequencies of low energy is of prime importance in the determination of thermodynamic functions for the heavier molecules and complicated systems. Problems that have puzzled spectroscopists for many years, in connection with discrepancies between spectroscopic and calorimetric quantities, are being unraveled by far infrared and Raman measurements. Good collections of spectra of research utility, like those of and proposed for the American Petroleum Institute Research Project 44 and the Manufacturing Chemists Association Research Project, are of considerable value to the working spectroscopist-thermodynamicist in determining thermodynamic properties.

APPARATUS AND TECHNIQUES

Any experimental measurement leading to a precise determination of a thermochemical, thermodynamic, or related physico-chemical property on a new class of substances poses new problems in apparatus, techniques, and in the interpretation of the experimental observations. In the area of thermochemistry, Jessup (63) presents a thorough discussion of the apparatus and procedures used at the National Bureau of Standards for the precise determination of heats of combustion of liquid hydrocarbons. Combustion calorimetry with fluorine is discussed by Armstrong & Jessup (64). Nuttall *et al.* (65) described an unusual glass combustion bomb for direct visual observation of the combustion reaction and of the effects of varied conditions. In the currently popular field of moving-bomb calorimetry, Sunner (66) discusses the combustion of sulfur compounds, Bjellerup (67, 68) that of organic bromine compounds including rigorous reduction of the data to standard states by the Washburn method, and McCullough (37) that of the heat of formation of aqueous sulfuric acid. Stout and his associates (69) describe in great detail their isothermal calorimeter for the measurement of low temperature heat capacities of solids and particularly their reduction procedure to obtain corrected heat capacities. They claim higher accuracy for the isothermal calorimeter than for many adiabatic calorimeters in the low temperature range and show, with measurements on the heat capacity of a standard sam-

ple of benzoic acid, that the National Bureau of Standards values are too low below 20°K. Kirshenbaum *et al.* (70) describe a procedure for determining heats of formation of substances such as O_2F_2 and O_3F_2 that decompose spontaneously at temperatures below 0°C.

Hall (71) who has pioneered in the area of high temperature—high pressure studies describes studies on the fusion curves for indium and tin. The perennial question concerning the existence of a liquid-solid critical point analogous to the gas-liquid critical point is brought up. Hall's results give no evidence for or against such a phenomenon. In the area of equation of state studies, Doolittle describes a procedure for precise determination of the compressibilities of liquid hydrocarbons (72). The method is applied to an extensive series of measurements on eight high purity liquid hydrocarbons in the C_7 to C_{40} range. A simple but effective gas densitometer for measuring thermal expansions of solid salts from room temperature to the melting point is described by Bockris *et al.* (73). A posthumous publication of Kobe's (74) discusses the Burnett method for determination of gas compressibilities. The well known temperature cell for the triple point of water developed by Stimson is now available commercially (75, 76) with a claimed accuracy of $\pm 0.0005^\circ\text{C}$. Badley (77) proposes a modified treatment of calorimetric data based on a heat content-temperature relation applicable to moderately non-ideal solutions for the calorimetric determination of purity of organic compounds.

SUBSTANCE-PROPERTY INDEX

The format adopted for summarizing published thermodynamic data is essentially the same as used in the past, consisting of three tables. Table I and Table II, respectively, list the well-defined inorganic and organic substances for which properties were measured or calculated. These substances are arranged in the standard order for the elements and compounds as used in the loose-leaf data sheets of the API Research Project 44 and the MCA Research Project. At the bottom of Table I, a code of key letters defines the particular properties measured or calculated for each substance and further delineates the kind of chemical thermodynamic information included in this survey. For further information regarding the standard order followed and the property code used, the reader is referred to the Introduction to the data catalog of the MCA Research Project. Table III, entitled Reaction Heats and Equilibria, lists chemical reaction equilibria studied where either heats or equilibrium constants or both were measured between well-defined chemical species and excludes reactions in solution where solvent effects are not negligible. Equilibrium studies leading to values of ΔH_f° and ΔF_f° are included in Tables I and II. The recent *IUPAC* nomenclature rules were used for the description column.

As has been the case in recent years, the tables illustrate much variety in the substances studied (305 inorganic and 176 organic entries), with practically every element represented in some form or another. The lag of publications resulting from government-classified or company-classified investiga-

tions is probably apparent. There is indeed a steady turnover of formerly classified material, but it may be some years before the real impact of the era connected with the conquest of space is felt in the field of published thermodynamic properties. Every encouragement to shorten this period, on an international basis, should be made.

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TABLE I
THERMODYNAMIC PROPERTIES MEASURED OR CALCULATED
INORGANIC COMPOUNDS

Formula	Description	State	Property*	Reference
O ₂	Oxygen	(c, liq, g)	agim	(12, 78, 79, 80)
H ₂	Hydrogen	(c, liq, g)	agijrstv	(12, 78; 81 to 84)
² H ₂	Deuterium	(c, liq, g)	agijrstv	(82, 83, 84)
H ₂ O	Water	(c, liq, g)	gijkrstv	(78, 85 to 91)
He	Helium	(liq, g)	agij	(12, 78, 92, 93, 94)
Ne	Neon	(c, liq, g)	aim	(78, 95)
²² Ne	Neon (²² Ne)	(c, liq, g)	am	(95)
Ar	Argon	(liq, g)	aijrt	(12, 78, 90)
Kr	Krypton	(c, liq, g)	im	(97)
Xe	Xenon	(c, liq, g)	ijmrt	(96, 97)
O ₂ F ₂	Dioxygen difluoride	(liq)	p	(70)
O ₃ F ₂	Trioxxygen difluoride	(liq)	p	(70)
HF	Hydrogen fluoride	(liq, g)	gpv	(64, 98, 99)
Br ₂	Bromine	(c)	m	(100)
BrF ₃	Bromine pentafluoride	(liq, g)	k	(101)
I	Monatomic iodine	(g)	prstv	(102)
I ₂	Iodine	(c, g)	prstv	(102, 103)
IF ₇	Iodine heptafluoride	(g)	rstv	(104)
S	Sulfur	(c, liq)	kmn	(37, 105, 106)

(Continued on next page)

*Code to Properties for Table I and Table II

- a. Density or specific volume, boiling point, freezing or triple point
- g. Compressibility
- i. Critical State Data
- j. P-V-T Data
- k. Vapor pressures
- m. Temperature, heat, and entropy of transition, fusion, and vaporization
- n. Heat of combustion
- p. Standard heat of formation (ΔH_f°), standard free energy of formation (ΔF_f°)
- r. Heat content or heat content function, $H^\circ - H_0^\circ$ or $(H^\circ - H_0^\circ)/T$ and $(H_{\text{solid}} - H_0^\circ)/T$
- s. Free energy function, $(F^\circ - H_0^\circ)/T$ or $(F_{\text{solid}} - H_0^\circ)/T$
- t. Entropy of gas, liquid, or solid; or entropy increments
- v. Heat capacity of gas, liquid, or solid

TABLE I—continued

Formula	Description	State	Property*	Reference
SO ₂	Sulfur dioxide	(liq)	i	(78)
H ₂ S	Hydrogen sulfide	(c)	gm	(107)
H ₂ SO ₄	Sulfuric acid and its hydrates	(c, liq)	rstv	(14)
SF ₄	Sulfur tetrafluoride	(g)	p	(108)
SF ₆	Sulfur hexafluoride	(liq)	aik	(109)
SO ₂ F ₂	Sulfonyl fluoride	(c, liq, g)	akmtv	(110)
S ₂ O ₂ Cl ₂	Pyrosulfuryl dichloride	(c, liq)	k	(111)
BrSO ₃ F	Bromine trioxofluorosulfate	(liq)	k	(112)
TeSe	Tellurium selenide	(g)	p	(113)
¹⁴ N ₂	Nitrogen	(liq, g)	agimt	(12, 78, 92, 114)
¹⁵ N ₂	Nitrogen (¹⁵ N ₂)	(g)	amt	(114)
NO	Nitrogen oxide and isotopes	(liq)	km	(115)
N ₂ O	Dinitrogen oxide	(c)	a	(116)
NH ₃	Ammonia	(c, liq, g)	gijkmrstv	(54, 78, 107, 117)
N ³ H ₃ , N ² H ₃	Ammonia (³ H ₃) and (² H ₃)	(g)	rstv	(55)
HNO ₃	Nitric acid	(c, liq, g)	agikmptv	(35)
NH ₄ NO ₃	Ammonium nitrate	(liq)	rstv	(118)
N ₂ F ₂	Difluorodiazine (<i>cis</i> and <i>trans</i>)	(c, liq, g)	aikm	(119)
NOF	Nitrosyl fluoride	(g)	p	(120)
NH ₄ ClO ₄	Ammonium perchlorate	(c)	p	(121)
P	Phosphorus	(c)	m	(122)
P ₄	Phosphorus	(g)	rstv	(57)
PH ₃ (H= ¹ H, ² H, ³ H)	Phosphine (¹ H ₃), (² H ₃), and (³ H ₃)	(g)	rstv	(54, 55)
POCl ₃	Phosphoryl trichloride	(c, liq, g)	akmrstv	(123)
AsH ₃ (H= ¹ H, ² H, ³ H)	Arsine (¹ H ₃), (² H ₃), and (³ H ₃)	(g)	rstv	(54, 55)
18 molecules of the type XYZ ₃ where (X=N, P or As) and (Y, Z= ¹ H, ² H, or ³ H)		(g)	rstv	(56)
SbH ₃	Stibine	(c, liq, g)	akm	(124, 125)
SbTe	Antimony telluride	(g)	p	(113)
SbCl ₃ , SbCl ₅	Antimony trichloride and pentachloride	(g)	rstv	(126)
BiF ₃	Bismuth pentafluoride	(c, liq, g)	akm	(127)
BiCl	Bismuth monochloride	(c, g)	kpt	(128, 129)
BiCl ₃	Bismuth trichloride	(c)	kmpt	(129, 130)
BiBr ₃	Bismuth tribromide	(c, g)	p	(131)
BiSe	Bismuth monoselenide	(g)	p	(113)
BiTe	Bismuth monotelluride	(g)	p	(113)
Bi ₂ Te ₃	Dibismuth tritelluride	(c)	mv	(132, 133, 134)
C ₃	Diatomic carbon	(g)	rstv	(135)
CO ₂	Carbon dioxide	(c, liq, g)	ai	(78, 116, 136)
CS ₂	Carbon disulfide	(g)	rstv	(137)
COS	Carbonyl sulfide	(g)	rstv	(137)
CSe ₂	Carbon diselenide	(g)	rstv	(137)
CSeS	Carbon selenide sulfide	(g)	rstv	(137)
Si	Silicon	(c)	rtv	(132, 138)
SiO ₂	Crystalline quartz	(c)	v	(139)
SiO ₂	Silicon dioxide	(g)	mprstv	(140, 141)
(SiH ₃ SiH ₃) ₂ O	<i>bis</i> (Disilanyl) ether	(liq)	k	(142)
SiF ₄	Silicon tetrafluoride	(c)	gm	(107)
SiH ₃ SiH ₃ I	Disilanyl iodide	(liq)	k	(142)
Si ₄ N ₄	Trisilicon tetranitride	(g)	pt	(143)
Ge	Germanium	(c)	v	(132)
GeH ₄	Germanium tetrahydride	(g)	rstv	(144)
GeX ₄ (X=F, Cl, Br, I)	Germanium halides	(g)	rstv	(144)
GeS	Germanium sulfide	(c)	k	(145)
Sn	Tin	(c, liq)	ajm	(71, 146)
Pb	Lead	(c, liq)	am	(147, 148)

TABLE I—continued

Formula	Description	State	Property*	Reference
PbO	Lead oxide	(c)	akmrtv	(149, 150, 151)
PbX ₂ (X = Cl, Br, I)	Lead halides	(c)	m	(152)
Pb(OH)I	Lead hydroxide iodide	(c)	rstv	(153)
PbS	Lead sulfide	(c)	k	(145)
PbSO ₄	Lead sulfate	(c)	rstv	(154)
PbSe	Lead selenide	(c)	k	(155)
PbSeO ₄	Lead selenate	(c)	p	(156)
PbTe	Lead telluride	(c)	k	(157)
B	Boron	(c)	mrstv	(158, 159)
B ₂ O ₃	Diboron dioxide	(g)	prstv	(160, 161)
B ₂ O ₅	Diboron trioxide	(c, g)	kmprstv	(161 to 164)
B ₂ H ₆	Diborane	(liq, g)	akmp	(164, 165, 166)
B ₁₀ H ₁₄	Decaborane	(c)	p	(167)
HBO ₂	Metaboric acid	(c, g)	prstv	(168, 169)
(HBO ₂) ₃	Trimetaboric acid	(g)	prstv	(169)
H ₂ BO ₃ ·1000H ₂ O	Orthoboric acid-1000 water	(aq)	p	(164)
BF ₃	Boron trifluoride	(g)	j	(170)
BF ₄ ⁻	Boron tetrafluoride ion	(g)	p	(171)
BCl ₃	Boron trichloride	(liq)	p	(164)
BClF ₂	Boron chloridedifluoride	(g)	p	(172)
BCl ₂ F	Boron dichloridefluoride	(g)	p	(172)
BH ₃ CO and isotopes ¹⁰ B, ¹¹ B, ¹ H, ² H	Boron trihydrogen carbonyls	(g)	rstv	(58)
Al ₂ O ₃	Dialuminum trioxide	(c)	v	(173)
AlF ₃	Aluminum trifluoride	(c)	km	(174)
Ga	Gallium	(c)	amtv	(175 to 178)
In	Indium	(c, liq)	ajmv	(71, 178, 179)
InSb	Indium antimonide	(c)	pv	(132, 180)
Tl	Thallium	(c)	m	(178, 181)
TlCl	Thallium monochloride	(c)	m	(182)
TlSe	Thallium selenide	(c)	km	(183, 184)
Tl ₂ Se	Dithallium selenide	(c)	km	(183, 184)
Tl ₂ Se ₃	Dithallium triselenide	(c)	km	(183, 184)
Zn	Zinc	(c)	m	(185)
ZnS	Zinc sulfide	(c)	k	(186)
ZnTe	Zinc telluride	(c)	k	(187)
Zn ₂ P ₂	Trizinc diphosphide	(c)	p	(188)
Mono, di, and triethylene diamine complexes of Zn ⁺² ; Ni ⁺² ; Co ⁺² ; Fe ⁺² ; Mn ⁺²		(c)	mpst	(189)
Cd	Cadmium	(c)	km	(185, 190)
CdX ₂ (X = Cl, Br, I)	Cadmium dihalides	(c)	kmrtv	(191, 192, 193)
CdTe	Cadmium telluride	(c)	k	(187)
Hg	Mercury	(liq)	gi	(78, 85)
Hg ₂ SO ₄	Dimercury sulfate	(c)	rstv	(194)
HgSe	Mercury selenide	(c)	v	(132)
Cu	Copper	(c)	ktv	(195, 196, 197)
Ag	Silver	(c, liq)	k	(198)
AgX(X = Cl, Br)	Silver halides	(c)	m	(152)
Ag ₂ S	Disilver sulfide	(c)	v	(132)
Ag ₂ SO ₄	Disilver sulfate	(c)	rstv	(199)
Ag ₂ Se	Disilver selenide	(c)	v	(132)
Ag ₂ SeO ₄	Silver selenate	(c)	t	(200)
Ag ₂ Te	Disilver telluride	(c)	v	(132)
AgNO ₃	Silver nitrate	(c)	m	(201)
Au	Gold	(c)	a	(12, 202)
Pt	Platinum	(c)	kmp	(203)

(Continued on next page)

TABLE I—continued

Formula	Description	State	Property*	Reference
PtO ₂	Platinum dioxide	(c)	k	(204)
PtF ₆	Platinum hexafluoride	(g)	rstv	(205)
IrO ₃ , Ir ₂ O ₃	Iridium trioxide, diiridium trioxide	(c)	k	(204)
OsF ₆	Osmium hexafluoride	(g)	rstv	(205)
Pd	Palladium	(c)	kmp	(203)
PdCl ₂	Palladium dichloride	(c)	k	(206)
RhO ₂	Rhodium dioxide	(c)	k	(204)
NiCl ₂ ·6H ₂ O	Nickel dichloride hexahydrate	(c)	mv	(207)
NiS	Nickel sulfide	(c)	prstv	(208)
Co	Cobalt	(c)	v	(209)
CoCl ₂ ·6H ₂ O	Cobalt dichloride hexahydrate	(c)	mv	(207)
Co _x S _y	Lower sulfides of cobalt	(c)	prstv	(208, 210)
[Co(NH ₂) ₂ N ₂](N ₃) ₂	Cobalt amine azides	(c)	mnp	(211)
[Co(NH ₂) ₂ Cl]Cl ₃	Chloropentamine cobalt (III) chloride	(c)	kmst	(212)
[Co(NH ₂) ₄]Cl ₃	Hexamine cobalt (III) chloride	(c)	kmst	(212)
[Co(NH ₂) ₄ OH ₂]N ₃	Aquopentamine cobalt (III) salts	(c)	p	(213)
(X = Br, NO ₂)				
[Co(NH ₂) ₄]N ₃ (X = Br, NO ₂ , ClO ₄)	Hexamine cobalt (III) salts	(c)	pt	(214)
FeX ₂ (X = Cl, Br, I)	Iron dihalides	(c)	k	(215)
Iron nitrides		(c)	p	(216)
Zinc ferrites		(c)	v	(217)
Mn	Manganese	(c, liq)	kv	(198, 209)
Manganese and its compounds		(c)	kmprtv	(34)
MnCl ₂ ·4H ₂ O	Manganese dichloride tetrahydrate	(c)	v	(218)
Manganese nitrides		(c)	p	(219)
Mn ₃ (CO) ₁₀	Decacarbonyldimanganese	(c)	km	(220)
Elements and compounds encountered in metallurgical reactions of Mn			pvt	(34)
ReX ₃ (X = Cl, Br)	Rhenium trihalides	(c)	p	(221)
MO ₃ (M = Ti, V, Cr, Zr, Nb, Mo, Hf, W, Ta)	Group IV, V, and VI oxides	(g)	s	(222)
CrO ₂ Cl ₂	Chromyl dichloride	(g)	rstv	(223)
CrBr ₂	Chromium dibromide	(c)	k	(224)
Cr ₂ N	Dichromium nitride	(c)	np	(225)
Cr(CO) ₆	Chromium hexacarbonyl	(g)	rstv	(226)
MoO ₃	Molybdenum dioxide	(c)	prtv	(227)
MoO ₃	Molybdenum trioxide	(c, liq)	prstv	(227)
MoF ₆	Molybdenum hexafluoride	(liq)	amprtv	(228, 229)
MoCl ₃	Molybdenum dichloride	(c)	np	(230)
MoCl ₃	Molybdenum trichloride	(c)	np	(230)
Mo ₂ N	Dimolybdenum nitride	(c)	np	(225)
Mo(CO) ₆	Molybdenum hexacarbonyl	(c, g)	kmrstv	(226, 231)
MoSi ₂ , Mo ₃ Si ₂ , and Mo ₅ Si ₃	Molybdenum silicides	(c)	kp	(232)
WO ₃	Tungsten dioxide	(c)	prtv	(227, 233)
WO ₃	Tungsten trioxide	(c, liq)	prtv	(227)
WF ₆	Tungsten hexafluoride	(g)	p	(228)
WBr ₃	Tungsten pentabromide	(c)	km	(234)
ZnWO ₄	Zinc tetroxowolframate	(c)	t	(235)
CoWO ₄	Cobalt tetroxowolframate	(c)	mv	(236)
Nb	Niobium	(c)	v	(173)
NbO, NbO ₂ , Nb ₂ O ₅	Niobium oxides	(c)	np	(237, 238)
NbF ₅	Niobium pentafluoride	(c)	amprtv	(228, 229)
NbCl ₅	Niobium pentachloride	(c)	p	(239)
NbC	Niobium carbide	(c)	p	(238)

TABLE I—continued

Formula	Description	State	Property*	Reference
TaCl ₅	Tantalum pentachloride	(c)	p	(239)
Ti	Titanium	(c)	rv	(240)
TiCl ₂	Titanium dichloride	(c)	mt	(241)
TiCl ₃	Titanium trichloride	(c)	mpt	(241, 242)
TiCl ₄	Titanium tetrachloride	(c)	a	(241)
TiBr ₄	Titanium tetrabromide	(g)	rstv	(243)
TiI ₄	Titanium tetraiodide	(c)	k	(244)
TiSi, TiSi ₂ , Ti ₃ Si ₂	Titanium silicides	(c)	rv	(240)
ZrCl ₂ , ZrCl ₃	Zirconium dichloride and trichloride	(c)	ptv	(245)
ZrCl ₄	Zirconium tetrachloride	(g)	rstv	(126)
HfCl _n (n = 2, 3, 4)	Hafnium chlorides	(c)	ptv	(245)
ScH ₂	Scandium dihydride	(c)	k	(246)
Lu	Lutetium	(c)	n	(247)
Lu ₂ O ₃	Dilutetium trioxide	(c)	p	(247)
Tm	Thulium	(c)	n	(248)
Tm ₂ O ₃	Dithulium trioxide	(c)	p	(248)
Tb	Terbium	(c)	v	(249)
Sm	Samarium	(c)	mrstv	(250, 251)
Nd	Neodymium	(c)	mrstv	(251)
Ce	Cerium	(c, liq)	mrstv	(251)
Ce ₂ O ₃	Dicerium trioxide	(c)	mp	(252)
LaCl ₃	Lanthanum trichloride	(c)	am	(253)
Pu	Plutonium	(liq)	a	(254)
PuF ₆	Plutonium hexafluoride	(c, liq)	km	(255)
Np	α -Neptunium	(c)	mv	(256)
NpF ₆	Neptunium hexafluoride	(c, liq)	km	(255)
U	α -Uranium	(c)	rstv	(257)
UO ₂	Uranium dioxide	(c)	m	(258)
V ₂ O ₅	Divanadium trioxide	(c)	m	(259)
U ₃ O ₈	Triuranium octoxide	(c)	v	(260)
U ²³⁵ H ₂	β -Uranium trideuteride	(c)	rstv	(261)
UF ₄	Uranium tetrafluoride	(liq, g)	kmpstv	(262 to 265)
UF ₆	Uranium hexafluoride	(c)	k	(255)
UCl ₄	Uranium tetrachloride	(c, liq)	amv	(266)
UOCl ₂	Uranium dichlorideoxide	(c)	p	(267)
UO ₂ Cl ₂	Uranyl dichloride	(aq)	p	(268)
UO ₂ Cl ₂ ·H ₂ O, UO ₂ Cl ₂ ·3H ₂ O	Uranyl dichloride monohydrate and trihydrate	(c)	p	(268)
UO ₂ Br ₂	Uranyl dibromide	(aq)	p	(268)
UO ₂ Br ₂ ·H ₂ O, UO ₂ Br ₂ ·3H ₂ O	Uranyl dibromide monohydrate and trihydrate	(c)	p	(268)
UI ₄	Uranium tetraiodide	(c, liq)	amv	(266)
UN	Uranium nitride	(c)	m	(258)
UC	Uranium carbide	(c)	m	(258)
UAl ₃ , UAl ₅ , UAl ₄	Uranium aluminides	(c)	p	(269)
Th	Thorium	(c)	v	(270)
ThF ₄	Thorium tetrafluoride	(c)	p	(271)
ThOF ₂	Thorium oxidedifluoride	(c)	p	(272)
ThI ₄	Thorium tetraiodide	(c)	p	(244)
Th(SO ₄) ₂	Thorium disulfate	(c)	ptv	(273)
Ac	Actinium	(c)	k	(274)
BeO	Beryllium oxide	(c)	rv	(275)
BeF ₂	Beryllium difluoride (β -Cristobalite)	(c)	kp	(276, 277)
BeCl ₂	Beryllium dichloride	(c)	a	(278)
Mg	Magnesium	(c)	v	(279)
MgH ₂	Magnesium dihydride	(c)	p	(280, 281)
Mg ² H ₂	Magnesium dideuteride	(c)	p	(281)

(Continued on next page)

TABLE I—continued

Formula	Description	State	Property*	Reference
MgNi ₂	Magnesium dinickelide	(c)	tv	(282)
MgFe ₂ O ₄	Magnesium tetroxodiferrate	(c)	p	(283)
MgWO ₄	Magnesium tetroxowolframate	(c)	v	(236)
CaF ₂	Calcium fluoride	(c)	v	(284)
CaSeO ₄	Calcium selenate	(c)	p	(285)
CaSeO ₄ ·2H ₂ O	Calcium selenate dihydrate	(c)	pt	(285, 286)
CaFe ₂ O ₄	Calcium tetroxodiferrate	(c)	p	(283)
CaWO ₄	Calcium tetroxowolframate	(c)	pv	(236)
CaZrO ₄	Calcium trioxozirconate	(c)	ptv	(287)
SrCl ₂ ·6H ₂ O	Strontium dichloride hexahydrate	(c)	m	(152)
SrS	Strontium sulfide	(c)	rstv	(288)
SrO·Al ₂ O ₃	Strontium oxide-trioxodialuminate	(c)	p	(289)
3SrO·Al ₂ O ₃	3 Strontium oxide-trioxodialuminate	(c)	p	(289)
4SrO·Al ₂ O ₃	4 Strontium oxide-trioxodialuminate (α and β)	(c)	p	(289)
SrZrO ₄	Strontium trioxozirconate	(c)	ptv	(287)
BaCl ₂ ·2H ₂ O	Barium dichloride dihydrate	(c)	m	(152)
BaBr ₂	Barium dibromide	(c)	m	(152)
BaS	Barium sulfide	(c)	rstv	(288)
BaSeO ₄	Barium selenate	(c)	p	(156)
BaZrO ₄	Barium trioxozirconate	(c)	ptv	(287)
Alkaline earth halides		(c)	m	(290)
Li	Lithium	(c, liq)	mtv	(291, 292)
Li ₂ O ₂	Lithium dioxide	(c)	kmp	(293, 294)
LiH	Lithium hydride	(c, liq)	v	(173)
LiOH	Lithium hydroxide	(c, g)	st	(295)
Li ₂ (OH) ₂	Dilithium dihydroxide	(g)	st	(295)
LiF	Lithium fluoride	(c, liq, g)	kmrstv	(296 to 299)
LiCl	Lithium chloride	(c, liq, g)	agmrstv	(152, 298; 300 to 303)
LiClO ₄	Lithium perchlorate	(c)	p	(121)
LiBr	Lithium bromide	(c, g)	mrstv	(152, 298, 300)
LiI	Lithium iodide	(g)	mrstv	(298, 300)
Li ₂ X ₂ (X = Cl, Br, I)	Lithium halide dimers	(c)	rstv	(304)
LiNO ₂	Lithium nitrite	(c)	a	(305)
LiAlO ₂	Lithium dioxoaluminate	(c)	rt	(306)
LiFeO ₂	Lithium dioxoferrate	(c)	rt	(306)
LiTiO ₂	Lithium trioxotitanate	(c)	rt	(306)
Na	Sodium	(c, liq, g)	aijkmrstv	(209; 307 to 312)
Na ₂ O	Disodium oxide	(c)	rv	(313)
NaOH	Sodium hydroxide	(c, liq)	amptv	(314)
NaF	Sodium fluoride	(c)	agmt	(299)
NaCl	Sodium chloride	(c, g)	agmrstv	(73, 298, 299, 300, 303)
NaBr	Sodium bromide	(c, g)	agmrstv	(152, 298, 299, 300, 303)
NaI	Sodium iodide	(c, g)	agmrstv	(152, 298, 299, 300, 303, 315)
Na ₂ S ₂ O ₇	Disodium pyrosulfate	(c, liq)	mv	(316)
NaHSO ₄	Sodium hydrogensulfate	(c, liq)	mv	(316)
NaNO ₃	Sodium nitrate	(c)	a	(305)
Na ₂ X(X = P, As, Sb, Bi)	Trisodium phosphide, arsenide, antimonide, and bismuthide	(c)	p	(317)
NaAlO ₂	Sodium dioxoaluminate	(c)	mt	(306)
NaFeO ₂	Sodium dioxoferrate	(c)	mt	(306)
Na ₂ CrO ₄	Sodium chromate	(c)	p	(318)
Na ₂ Cr ₂ O ₇	Sodium dichromate	(c)	p	(318)
K	Potassium	(c, liq)	kmtv	(309, 311)
KF	Potassium fluoride	(c)	mtv	(299, 319)

TABLE I—continued

Formula	Description	State	Property*	Reference
KCl	Potassium chloride	(c, g)	agkmrstv	(73, 298, 299, 300, 303, 319, 320, 321)
KClO ₄	Potassium perchlorate	(c)	p	(121)
KBr	Potassium bromide	(c, g)	mrvst	(152, 298, 299, 300, 319)
KI	Potassium iodide	(c)	mtv	(152, 299, 300, 319)
KCNS	Potassium thiocyanate	(c, liq)	m	(322)
KBF ₄	Potassium tetrafluoroborate	(c)	p	(171)
K ₂ MoO ₄	Dipotassium tetroxomolybdenate	(c)	p	(318)
K ₂ TiF ₆	Dipotassium hexafluorotitanate	(c)	mp	(323)
KNa	Potassium sodiumide	(liq)	k	(311)
RbF	Rubidium fluoride	(c)	mv	(300, 319)
RbCl	Rubidium chloride	(c, g)	agmrstv	(298, 300, 303, 319)
RbBr	Rubidium bromide	(c)	mtv	(299, 300, 319)
RbI	Rubidium iodide	(c)	mv	(300, 319)
CsF	Cesium fluoride	(c)	mv	(300, 319)
CsCl	Cesium chloride	(c, g)	agmrstv	(298, 300, 303)
CsX (X = Br, I)	Cesium halides	(c)	m	(300)
CsNO ₃	Cesium nitrate	(c)	a	(305)
Alkali halides		(c)	m	(290)
36 Elements between Lithium and Uranium		(liq)	ik	(324)
88 Elements	Unipositive ions	(g)	rstv	(325)

TABLE II
THERMODYNAMIC PROPERTIES MEASURED OR CALCULATED
ORGANIC COMPOUNDS

Formula	Description	State	Property*	Reference
CH ₄	Methane	(c, liq)	gkm	(79, 97, 326)
C ² H ₄	Tetradeuteromethane	(c)	gm	(79)
12 Methanes with ¹ H, ² H and ³ H		(g)	rstv	(327)
¹³ CH ₄	Methane (¹³ C)	(liq)	k	(326)
C ₂ H ₆	Ethane	(g)	jprstv	(328)
C ₅ H ₁₂	<i>n</i> -Pentane	(liq)	imr	(329, 330, 331)
	Isopentane	(g)	j	(332)
	Neopentane	(liq)	i	(330)
C ₆ H ₁₄	<i>n</i> -Hexane	(liq)	i	(330)
C ₇ H ₁₆	<i>n</i> -Heptane	(liq)	m	(333)
	Isomeric heptanes	(liq)	mp	(334, 335)
C ₈ H ₁₈	<i>n</i> -Octane	(liq, g)	gjm	(333, 336)
	Ethylhexanes	(liq)	m	(334)
	Dimethylhexanes	(liq)	m	(334)
Normal Alkanes C ₁ to C ₈ and C ₁₂		(liq)	i	(78)
Normal Alkanes C ₇ , C ₈ , C ₁₁ , C ₁₅ , C ₁₇ , C ₂₀ , C ₂₅ and C ₂₈		(liq)	ag	(72)
C ₃ H ₆	Cyclopropane	(liq, g)	jm	(337, 338)
C ₇ H ₁₄ , C ₈ H ₁₆ , C ₁₁ H ₂₂	1,1-Dimethyl-2- <i>n</i> -alkyl cyclopropanes (alkyl = ethyl, propyl, hexyl)	(liq)	np	(339)
C ₄ H ₈	Cyclobutane	(liq)	m	(338)
C ₅ H ₁₀	Cyclopentane	(liq)	m	(338)

* Code to Properties on page 333.

(Continued on next page)

TABLE II—continued

Formula	Description	State	Property*	Reference
C ₅ H ₁₂	Methylcyclopentane	(g)	prstv	(340)
C ₇ H ₁₄	1, <i>cis</i> -3-Dimethylcyclopentane	(g)	prstv	(340)
C ₁₀ H ₁₈	<i>n</i> -Decylcyclopentane and <i>n</i> -alkyl cyclopentanes (alkyl = propyl and higher)	(liq)	mnp	(27)
C ₆ H ₁₂	Cyclohexane	(c, liq, g)	ijm	(337, 338, 341)
C ₇ H ₁₄	Methylcyclohexane	(liq)	k	(342)
C ₈ H ₁₆	Ethylcyclohexane	(liq)	k	(342)
C ₉ H ₁₈ , C ₁₀ H ₂₀ , C ₁₁ H ₂₂	<i>n</i> -Alkylcyclohexanes (alkyl = propyl, butyl, decyl)	(liq)	k	(342)
C ₁₀ H ₂₀	<i>n</i> -Decylcyclohexane and <i>n</i> -alkyl cyclohexanes (alkyl = propyl and higher)	(liq)	mnp	(27)
C ₇ H ₁₄ —C ₁₀ H ₂₀	Cycloheptane through cyclodecane	(liq)	m	(338)
C ₁₂ H ₂₄	1,1-Dicyclohexyldodecane	(c)	amprtv	(343, 344)
C ₈ H ₁₆	Hexahydroindans (<i>cis</i> and <i>trans</i>)	(liq, g)	mnp	(26)
C ₁₀ H ₁₈	Decahydronaphthalenes (<i>cis</i> and <i>trans</i>)	(liq, g)	mnp	(29)
C ₁₀ H ₁₈	9-Methyl decahydronaphthalenes (<i>cis</i> and <i>trans</i>)	(liq)	mp	(345)
C ₁₀ H ₁₆	Tricyclo[3·3·1·1 ⁰ ·7]decane (Adamantane)	(c, liq)	mprstv	(346)
C ₃ H ₆	Propene	(g)	v	(347)
C ₆ H ₁₂	The 17 isomeric hexenes	(liq, g)	mnp	(28)
C ₇ H ₁₄	3-Methyl-3-hexenes (<i>cis</i> and <i>trans</i>)	(liq)	akm	(348)
	2,4-Dimethyl-1 and 2,4-Dimethyl-2-pentenes	(liq)	akm	(348)
	4,4-Dimethyl-1 and <i>cis</i> and <i>trans</i> -4,4-Dimethyl-2-pentenes	(liq)	akm	(348)
	3-Methyl-2-ethyl-1-butene	(liq)	akm	(348)
	2,3,3-Trimethyl-1-butene	(liq)	akm	(348)
C ₆ H ₁₀	2,2-Dimethyl-3-hexenes (<i>cis</i> and <i>trans</i>)	(liq)	akm	(348)
	2-Methyl-3-ethyl-1-pentene	(liq)	akm	(348)
	2,4,4-Trimethyl-1 and 2,4,4-trimethyl-2-pentenes	(liq)	akm	(348)
C ₁₆ H ₃₂	1-Hexadecene and 1- <i>n</i> -alkenes from 1-propene and higher	(liq)	mnp	(27)
C ₇ H ₁₂	1-Methylcyclohexene	(liq)	akm	(348)
C ₈ H ₁₄	1-Ethylcyclohexene	(liq)	akm	(348)
C ₄ H ₆	Propyne (Methylacetylene)	(g)	j	(332)
C ₆ H ₆	Benzene	(c, liq, g)	gijmrstv	(331, 336, 337, 341, 349)
C ₆ D ₆	Hexadeuterobenzene	(g)	rstv	(349)
C ₇ H ₈	Toluene (Methylbenzene)	(liq, g)	irstv	(349)
C ₇ D ₈	Octadeuterotoluene	(g)	rstv	(349)
C ₆ H ₁₂	4 Isomeric benzenes	(liq)	a	(350)
C ₁₀ H ₁₈	<i>n</i> -Decylbenzene and <i>n</i> -alkylbenzenes (alkyl = propyl and higher)	(liq)	mnp	(27)
C ₁₁ H ₂₀	1-Cyclohexyl-1-phenyldodecane	(c)	mrtv	(344)
C ₁₂ H ₂₂	Diphenylmethane	(c)	km	(351)
C ₁₄ H ₁₄	1,2-Diphenylethane (Bibenzyl)	(c)	km	(351)
C ₁₄ H ₁₄	1,1-Diphenyldodecane	(c)	kmrstv	(344)
C ₁₀ H ₁₆	Triphenylmethane	(c)	km	(351)
C ₁₂ H ₁₀	Biphenyl	(c, g)	kmrstv	(351, 352)
C ₁₂ D ₁₀	Decadeuterobiphenyl	(g)	rstv	(352)
C ₁₀ H ₈	Naphthalene	(c, liq, g)	kmnp	(29, 351, 353)
C ₁₁ H ₁₀	1- <i>n</i> -Alkyl naphthalenes (alkyl = methyl and higher)	(liq, g)	mnp	(29)
	2- <i>n</i> -Alkyl naphthalenes (alkyl = methyl and higher)	(c, liq, g)	mnp	(29)
C ₁₂ H ₁₂	2,3 and 2,6-Dimethylnaphthalenes	(c)	km	(351)
C ₈ H ₁₀	Ethynylbenzene	(g)	rstv	(354)
13 very pure hydrocarbons (cycloalkanes, alkenes, cycloalkenes, benzenes, alkyldiene cycloalkanes)		(c)	a	(355)
29 very pure hydrocarbons (alkanes, cycloalkanes, alkenes, aromatics)		(liq)	i	(356)

TABLE II—continued

Formula	Description	State	Property*	Reference
HCO	Formyl radical	(g)	rstv	(357)
CH ₃ OH	Methanol	(liq)	kp	(358, 359, 360)
C ₂ H ₅ OH	Ethanol	(liq)	kpr	(331, 358, 360)
C ₃ H ₇ OH	1-Propanol	(liq)	kp	(358, 360, 361)
	2-Propanol	(liq)	k	(358)
C ₄ H ₉ OH	1-Butanol	(liq)	knp	(358, 360, 361, 362)
	2-Butanol	(liq)	k	(358)
	2-Methyl-1-propanol	(liq)	k	(358)
C ₅ H ₁₁ OH-C ₈ H ₁₇ OH	1-Pentanol through 1-octanol	(liq)	p	(360)
C ₆ H ₁₃ OH	2-Ethyl-1- and 2-ethyl-2-hexanols	(liq)	n	(362)
C ₉ H ₁₉ OH	1-Nonanol	(liq)	p	(360)
	3,5,5-Trimethylhexanol	(liq)	np	(363)
C ₁₀ H ₂₁ OH	1-Decanol	(liq)	p	(360)
HCHO	Formaldehyde	(g)	rstv	(364)
CH ₃ CHO	Acetaldehyde	(g)	rstv	(365)
C ₃ H ₇ CHO	1-Propanal	(g)	rstv	(365)
C ₄ H ₇ CHO	1-Butanal	(liq, g)	nprstv	(362, 365, 366)
C ₆ H ₁₁ CHO	1-Heptanal	(liq)	np	(366)
HCOOH	Formic acid	(c)	np	(367)
C ₈ H ₁₇ COOH	Nonanoic acid	(liq)	k	(368)
	2-Ethylheptanoic acid	(liq)	k	(368)
H ₂ C=C=O, ² H ₂ C=C=O	Ketene and dideuteroketene	(g)	rstv	(59)
CH ₃ CH(OH)COOH	Lactic acid	(c)	n	(369)
C ₄ H ₈ O	2-Butenal	(liq)	n	(362)
C ₆ H ₁₂ H ₂ O	2,2,4,4-Tetradeuterocyclobutanone	(g)	rstv	(370)
C ₄ H ₈ O	Tetrahydrofuran	(liq)	k	(371)
C ₆ H ₁₀ O	Cyclohexanol	(liq)	k	(372)
C ₇ H ₆ O ₂	Benzoic acid	(c)	n	(12, 26, 373)
C ₈ H ₁₄ O	2-Ethyl-2-hexenal	(liq)	n	(362)
C ₁₀ H ₁₈ O ₂	Benzoyl acetone	(c)	km	(351)
C ₁₂ H ₁₈ O	2-Acetylnaphthalene	(c)	km	(351)
C ₁₂ H ₁₀ O	Benzophenone	(c)	n	(374)
C ₁₄ H ₁₈ O ₂	Benzil	(c)	km	(351)
C ₁₄ H ₁₈ O	<i>p</i> -Methylbenzophenone	(c)	n	(374)
C ₁₅ H ₁₈ O-C ₁₇ H ₃₀ O	<i>p</i> -Alkylbenzophenones (Alkyl = ethyl, isopropyl, tert-butyl)	(liq)	n	(374)
5 Steroidal hydrindanones		(liq)	mp	(375)
CF ₄	Tetrafluoromethane	(c, liq, g)	gmprsv	(107, 376)
C ₆ F ₈	Perfluorocyclobutane	(g)	v	(347)
C ₆ F ₁₀ O	Perfluoro[2- <i>n</i> -butyltetrahydrofuran]	(g)	ajrt	(377)
CHF ₃	Trifluoromethane (Fluoroform, Freon 23)	(g)	rstv	(378)
C ₆ H ₆ F	Fluorobenzene	(liq)	i	(356)
CCl ₄	Tetrachloromethane	(c, liq, g)	gmprsv	(85, 376)
C ₆ Cl ₆	Lindane (Hexachlorobenzene)	(c)	a	(379)
CH ₃ Cl	Trichloromethane (Methyl chloride)	(liq)	i	(78)
C ₃ H ₅ Cl	Allyl chloride	(liq)	k	(380)
C ₃ H ₇ Cl ₃	1,2,3-Trichloropropane	(liq)	k	(381)
C ₃ H ₇ Cl	2-Chloropropane	(liq)	k	(380)
C ₃ H ₅ ClO	Epichlorohydrin	(liq)	k	(381)
CClF ₃	Chlorotrifluoromethane (Freon 11)	(c, liq, g)	prsv	(376)
CCl ₂ F ₂	Dichlorodifluoromethane (Freon 12)	(c, liq, g)	iprstv	(78, 376, 378)
CCl ₃ F	Trichlorofluoromethane (Freon 13)	(c, liq, g)	prsv	(376)

(Continued on next page)

TABLE II—continued

Formula	Description	State	Property*	Reference
$C_2Cl_2F_4$	Dichlorotetrafluoroethane	(liq, g)	aipkv	(382)
CBr_4	Tetrabromomethane	(c)	ak	(383)
CBr_2Cl_2F	Bromodichlorofluoromethane	(liq, g)	rstv	(60)
$CBBr_2ClF$	Dibromochlorofluoromethane	(liq, g)	rstv	(60)
$C_2H_2I_2$	Diiodoethene	(g)	rstv	(384)
10 organic Sulfur compounds (Alkanethiols, thiaalkanes and benzene-thiol)		(liq)	a	(385)
CF_3SH	Trifluoromethanethiol	(c, liq)	akmtv	(386)
CaN_2	Dicyanoacetylene	(liq)	np	(387)
CH_3CN	Ethanenitrile	(g)	rstv	(61)
CH_3NC	Methyl isocyanide	(g)	rstv	(61)
$(CH_3)_2N_2H_2$	1,1-Dimethylhydrazine	(liq)	np	(388)
$CaN_3(NH_3)_3$	2,4,6-Triamino- <i>s</i> -triazine (Melamine)	(c)	km	(389)
CaH_2N_4	Hexamethylenetetramine (1,3,5,7-Tetraazatricyclo[3.3.1.1 ^{3,7}]decane)	(c, liq)	prstv	(346)
$(CH_3)_4N_4$	Tetramethyl-2-tetrazene	(liq)	np	(388)
CaH_5N	Pyridine	(liq)	i	(356)
$NC(CH_2)_nCN$ ($n=3$ to 8)	6 α,ω -Dinitriles	(liq)	ak	(390)
CaH_7N	3 Picolines	(liq)	i	(356)
CaH_8N_2	Triethylenediamine (1,4-Diazabicyclo-[2.2.2]octane)	(c)	akmrstv	(391, 392)
$CaH_{11}NH_2$	Cyclohexylamine	(liq)	k	(372)
$(C_2H_5)_3N$	Triethylamine	(liq)	n	(393)
C_7H_7N	2-Vinylpyridine	(liq)	n	(394)
C_7H_9N	2-Ethylpyridine	(liq)	n	(394)
	6 Lutidines (2, 3; 2, 4; 2, 5; 2, 6; 3, 4; 3, 5)	(liq)	ijmp	(356, 395)
$CH_2(NH_2)COOH$	Glycine	(c, liq)	rstv	(396)
CaH_4NaO_3	Glyceryl trinitrate (Nitroglycerin)	(c)	km	(397)
$CH_3CH(NH_2)COOH$	<i>L</i> -Alanine	(c, liq)	rstv	(396)
CaH_4NaO_{11}	Nitroisobutanetriol trinitrate	(c)	km	(397)
$(O_2NOCH_2CH_2)_2O$	Diethylene glycol dinitrate	(c)	km	(397)
CaH_4NO_3	Nitrobenzene	(liq)	k	(398)
$CaH_{12}N_2O_3$	Hexamethylene diisocyanate	(liq)	akm	(399)
$CaH_4N_2O_3$	2,4-Toluene diisocyanate	(liq)	akm	(400)
5-N-substituted amides	N-Methyl-N-ethylpropionamide and 4 N-Methyl lactams (4 to 7 C atoms in ring)	(liq)	an	(401)
$(CaH_5)_3P$	Triethylphosphine	(liq)	n	(393)
$(C_6H_5)_3P$	Triphenylphosphine	(c)	np	(402)
$(CH_3)_3PO$	Trimethylphosphine oxide	(c)	p	(403)
$(C_6H_5O)_3PO$	Triethyl phosphate	(liq)	np	(409)
$(CaH_5)_3PO$	Triphenylphosphine oxide	(c)	np	(402)
CH_3POX_3 ($X=F, Cl$)	Methyl phosphoryl dihalides	(liq)	ak	(404)
$(CH_3)_2PNC_2H_5$	Trimethylphosphoro-N-ethylimine	(liq)	kmp	(403)
$(CaH_5)_2PNC_2H_5$	Triphenylphosphoro-N-ethylimine	(c)	p	(403)
$[CH_2N \cdot PCl_2]_3$	<i>bis</i> (Trichlorophosphoro-N-methylimine)	(c)	p	(405)
$(CaH_5)_3M$ ($M=As, Sb, Bi$)	Triethylarsine, stibine, and bismuth	(liq)	n	(393)
$(CH_3)_4Si$	Tetramethylsilane	(g)	rstv	(406)
$(CH_3)_6Si_2$	Hexamethyldisilane	(c, liq, g)	kmtv	(407)
8 organic silicates		(c)	anp	(408, 409)
$(CH_3)_2SiCl_2$	Dimethyldichlorosilane	(g)	rstv	(410)
$(CH_3)_3SiCl$	Trimethylchlorosilane	(g)	rstv	(411)
PbC_2O_4	Lead oxalate	(c)	pstv	(412)
R_3B ($R=Et, Pr$)	Trialkylboranes	(liq)	anp	(413)
$CaH_4B_2H_6$	Ethylidiborane	(liq)	k	(414)
$(CH_3O)_3B$	Methyl borate	(liq, g)	gjk	(415)

TABLE II—continued

Formula	Description	State	Property*	Reference
$B_2N_2(C_6H_5)_2H_2$	Triethyl borazine	(liq)	k	(416)
$(CaHg)_2M$ (M = Zn, Cd, Hg)	Diethyl zinc, cadmium, and mercury	(liq)	n	(393)
$(C_6H_5)_2Fe$	Ferrocene (Dicyclopentadienyl iron)	(c, liq)	amv	(417)
$Hf(OC_4H_9)_4$ and $Hf(OC_6H_{13})_4$	Hafnium tetrabutoxide and tetrapentyloxide	(c)	km	(418)
$HCOONa$	Sodium formate	(c)	ratv	(419)

TABLE III
REACTION HEATS AND EQUILIBRIA

Reaction	Reference
$O_2(g) + Ni(c) = O_2(a)$	(420)
$O_2(g) + \text{Evaporated metal films}(c) = O_2(a)$	(421)
$H_2(g) + Pt \text{ Black}(c) = H_2(a)$	(422)
$H_2(g) + M(c) = H_2(a)$	(423)
$H_2O(g) + \text{Graphitic oxide}(c) = H_2O(a)$	(424)
$\{N_2, Ar, Ne, o\text{-}^2H_2, p\text{-}H_2, He\}(g) + \text{Graphon}(c) = \{N_2, Ar, Ne, o\text{-}^2H_2, p\text{-}H_2, He\}(a)$	(425)
$N_2(g) + W(c) = N_2(a)$	(426)
$1/2 H_2O(g) + 1/2 B_2O_3(c) = HBO_2(g)$	(427)
$CdAs_2(c) = 1/3 Cd_3As_2(c) + 1/3 As_4(g)$	(428)
$CdAs_2(c) = 3Cd(g) + 1/2 As_4(g)$	(428)
$RuCl_3(c) = Ru(c) + 3/2 Cl_2(g)$	(429)
$2MX_2(g) = M_2X_4(g)$ for 9 transition metal halides (FeI ₂ and chlorides and bromides of Cr, Mn, Co, and Ni)	(430)
$Fe_2O_3(c) + 3H_2(g) = 2Fe(c) + 3H_2O(g)$	(431)
$3Fe_2O_3(c) + H_2(g) = 2Fe_3O_4(c) + H_2O(g)$	(431)
$Fe_3O_4(c) + 4H_2(g) = 3Fe(c) + 4H_2O(g)$	(431)
$2Fe^{3+}(aq) + H_2O_2 + 2H^+(aq) = 2Fe^{2+}(aq) + H_2O(liq)$	(432)
Reactions of compounds of manganese	(34)
$CrBr_3(c) + 1/2 Br_2(g) = CrBr_4(g)$	(433)
$Li_2O(c) + H_2O(g) = 2LiOH$; or $Li_2(OH)_2$	(295)
$Na_2Cr_2O_7(c) + 2OH^-(aq) = 2Na^+(aq) + 2CrO_4^{2-}(aq) + H_2O(liq)$	(318)
$MNO_3(liq) = MNO_2(liq) + 1/2 O_2(g)$ (M = Na and K)	(434)
Isomerizations of hexane isomers (liq)	(435)
<i>cis</i> -Hydrindan (liq) = <i>trans</i> -hydrindan (liq)	(436)
(Isoalkanes, naphthenes, toluene)(g) + Graphited carbon black(c) = (Isoalkanes, naphthenes, toluene)(a)	(437)
<i>cis</i> -Cycloalkene(soln) = <i>trans</i> -cycloalkene(soln) (C ₈ to C ₁₂)	(438)
(Benzene, <i>n</i> -hexane)(g) + Mg(OH) ₂ (c) = (Benzene, <i>n</i> -hexane)(a)	(439)

In the above 3 tables (a) refers to the adsorbed species; (g) refers to gas form; (c) refers to condensed form; (liq) refers to liquid form; (aq) refers to aqueous solution; (soln) refers to solution.

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HIGH TEMPERATURE CHEMISTRY^{1,2}

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Although man has been using fires for many millenia, high temperature chemistry, as it is now generally recognized, began about 1943. At that time, the U. S. Atomic Energy Commission was seeking high temperature materials for some of its metallurgical operations. During subsequent years the field grew rapidly. Several universities have active research and training programs. In Atomic Energy Commission laboratories and in other laboratories concerned with the space age, considerable effort is now in progress. Industry, largely because of government contracts, is pursuing the field actively. Since the last review the field has achieved a considerable degree of maturity, as evidenced by a rather large number of books, a huge number of research contracts for work in high temperature science, a voluminous literature, and many conferences.

The first review of high temperature chemistry by Brewer & Searcy (1), published in 1956, defined high temperature chemistry, described the status on high temperature gaseous species and the dissociation energies of important diatomic gases, and discussed the properties of complex oxide phases, metallic interstitial compounds, and ternary phases. The second review by Margrave (2) discussed new methods for measuring and attaining temperatures, kinetics of high temperature reactions, structural studies, high temperature syntheses, and thermodynamic properties of high temperature materials. Porter (3), also in 1959, in his report on heterogeneous equilibria, discussed vaporization reactions and tabulated vaporization results. Fused salts were discussed last year by Blomgren & Van Artsdalen (4) as were combustion and flames by Penner & Jacobs (5).

The progress during the past two years appears to have consisted mostly in accumulating urgently needed basic data; little theory was produced; a few techniques were developed; and some generalizations were made. It will be convenient to divide the following discussion into these parts: publications and conferences, theory, temperature measurement, techniques and apparatus, and experimental studies principally in the area of vaporization processes. Fused salts and flames will not be discussed.

PUBLICATIONS

Bockris, White & Mackenzie (6) have edited a book that is primarily concerned with experimental techniques and physical chemical measure-

¹ The survey of literature pertaining to this review was completed December 24, 1960.

² The author gratefully acknowledges the support of this work by the Division of Research of the United States Atomic Energy Commission under contract AT(11-1)-83, Project No. 1, with the University of Kansas.

ments in the temperature range of 1000–2000°C. The book attacks the basic problems in high temperature chemistry: choosing the materials for the apparatus, securing the high temperature, measuring the temperature, and making high temperature measurements. Kingery (7) has written a textbook that concerns much of the field of high temperature chemistry, with emphasis on the metallurgical and ceramic area. These two books, along with those by Lewis *et al.* (8), Wagner (9), and Darken & Gurry (10), and those edited by Campbell (11), Lebeau & Trombe (12), and the Stanford Research Institute (13), will form the textbook nucleus of any high temperature program. Gaydon & Wolfhard (14) have published a revised edition of their book on flames.

Properties and data for high temperature substances appeared in several publications. Kelley (15) revised his publication on high temperature heat capacity and entropy data. Levin & McMurdie (16) published the 1959 supplement to the well known compilation of phase diagrams for ceramists. Tipton (17) has edited volume I of the new enlarged reactor handbook. Volume II, part 2, of Landolt-Bornstein (18) has appeared and covers vapor-condensed phase equilibria and osmotic phenomena. These books, together with the other ones from Kelley's laboratory (19, 19a), NBS Circular 500 (20), Hansen (21), Pearson (22), Schwarzkopf & Kieffer (23), Herzberg (24), Gaydon (25), Sutton (26), Rosen (27), Kubaschewski & Evans (28), Stull & Sinke (29), Kolsky, Gilmer & Gilles (30), and the earlier edition of phase diagrams (31) will provide much of the ready reference material for high temperature laboratories.

Two new series of review volumes began in 1959. *Advances in Inorganic Chemistry and Radiochemistry* contained a lattice energy paper by Waddington (32) in volume I and an actinide halide paper by Katz & Sheft (33) in volume II. Volume II of *Modern Materials, Advances in Development and Applications* (34) contained two papers on the borides. Aronsson (35) discussed the basic factors and Steinitz (36) discussed the fabrication, properties and applications.

Two new journals also appeared: the *Journal of Nuclear Materials* (37) and the *Journal of the Less-Common Metals* (38). The *Journal of Nuclear Energy* was divided into three parts: Part A—Reactor Science; Part B—Reactor Technology; and Part C—Plasma Physics, Accelerators, Thermo-nuclear Research.

Several serial publications by various agencies contain high temperature data. The U.S. NBS issues reports on the thermodynamic properties of selected light element compounds (39) and on the thermochemistry and thermodynamic functions of boron compounds (40). Hultgren and others (41) are continuing with their publication of Selected Values of Thermodynamic Properties of Metals and Alloys. The Defense Information Center at Battelle Memorial Institute issues summaries of data on refractory metals and alloys and the state of the art of their fabrication in two sets of pamphlets the green-bound reports and the blue-bound memoranda (42).

The extremely large effort in nuclear energy development and space travel yields a huge number of technical reports. Brewer has issued short papers on heats of sublimation of the elements (43), dissociation energies of gaseous oxides (44), (with Rosenblatt) dissociation energies for gaseous metal dioxides (45) and (with Chandrasekhariah) free energy functions for gaseous oxides (46, 47). There are thermochemical tables prepared for the joint U. S. Army, Navy, and Air Force (48). Goldsmith, Waterman & Hirschhorn (49) have published volume I of their tabulation of the thermophysical properties of solid materials. Hildenbrand (50) has issued tables of thermodynamic data for performance calculations in connection with metal additives with solid propellants. The list could go on and on. Some of these reports will produce papers in the regular scientific literature, but most will not. About the only hope one has of keeping abreast of such developments is to watch Nuclear Science Abstracts and the Technical Abstract Bulletin of the Armed Services Technical Information Agency (51).

Also appearing are no fewer than eleven bibliographies (52 to 62). A list of bibliographies prepared by the Office of Technical Services of the U. S. Department of Commerce is available (63).

There were several conferences on topics as follows: high temperature technology, in California (13); metallic solutions and intermetallic compounds, in England (64); kinetics of high temperature processes, in Massachusetts (65); high temperature materials, in Cleveland (66); peaceful uses for atomic energy, in Geneva (67); thermodynamic and transport properties, in Indiana (68); high melting metals, in Austria (69); high temperature chemistry, in Paris (70); the properties of refractory metals, in England (71); the pyrometric temperature scale, at the U.S.NBS (72); and experimental techniques and methods of investigation in U.S.S.R. (73). The first Gordon Research Conference on high temperature chemistry was held in the summer of 1960, but, according to custom, no proceedings were published. The IUPAC scheduled a symposium on high temperature chemistry for the Montreal meeting in the summer of 1961, and the third symposium on *Temperature, Its Measurement and Control in Science and Industry* was scheduled for March, 1961 in Columbus.

THEORY

Quantum chemistry.—Pitzer & Clementi (74) have used molecular orbital theory to attack the long-standing problem of carbon vapor. Using their theory and the known trimer to monomer ratio, they predicted an even-odd alternation in the saturated pressures as the polymer number increases, with the odd ones being more abundant. The proportions of higher polymers were predicted to increase rapidly with temperature. For example, C_5 is predicted to be the most important gas at 2000°K., C_7 at 3000°K., and C_{13} at 4000°K. They also consider the effect of the size of the effusion hole on the experimental results. Motivated by this work, Drowart *et al.* (75) examined again the evaporation of graphite in a mass spectrometer. In agreement with the

prediction, they found that C_3 and C_1 are more important than C_2 and that C_5 is more important than C_4 , but C_5 , instead of being the most important species at 2000°K., was found to be about 10^{-3} as abundant as C_3 . The species C_6 and C_7 were not observed and were estimated to be less than 5×10^{-4} as abundant as C_1 at 2500°K., instead of being the major species. The vaporization coefficients for C_4 and C_5 appeared to be nearly unity. In spectroscopic studies of C_3 in equilibrium with graphite, Engelke (76) finds results in agreement with those from mass spectrometer investigations.

The discrepancy between experiment and theory could be made to disappear if the vaporization coefficient changed from nearly unity for C_5 to considerably less than 10^{-4} for C_7 , but this drastic change would itself require considerable explanation. A reliable measurement of the triple point or even a direct measurement of the sublimation point for the substance would be of great help.

Clementi & Pitzer (77) have also calculated, by a semi-empirical treatment, the energies of the low states of $C_2(g)$. The recent work of Ballik & Ramsay (78) has unequivocally established the ground state of C_2 to be $^1\Sigma_g^+$ instead of $^3\Pi_u$. Brounshtein & Yurkov (79) have also treated C_2 and TiO.

Attempts at the correlation of molecular dissociation energies have been discussed by Berkowitz (80) who examined isoelectronic reactions and by Somayajulu (81) who used a simple rule involving the dissociation energy, the equilibrium inter-nuclear distance, and the vibrational force constant.

A somewhat different approach to the problem of dissociation energies and the molecular energy level diagram has been taken by Berg & Sinanoglu (82) who used a ligand-field theory for oxides and halides of the first transition period.

Statistical mechanics.—It is customary in the calculation of the thermodynamic properties of gases from statistical mechanical techniques to evaluate the partition functions for the atoms and the molecules from spectroscopic data. Sinanoglu & Pitzer (83) have pointed out that, if the binding energies are low or if the temperatures are very high, the anharmonicity and distortion corrections are very high and not easily treated. They have suggested that it is more appropriate in such situations to regard the gas as consisting of atoms whose tendencies to coalesce are revealed by the potential energy curve. They have chosen the Rydberg potential for their treatment.

The effusion method.—Although the majority of high temperature thermodynamic data are obtained through the use of the Knudsen effusion method and although this method has been known for a long time, many of its aspects have not yet been clarified. Among these are: the corrections to be applied for the shape of the effusion hole, the corrections to be applied for the shape of the crucible, the effect of the location of the evaporating surface, the distribution of molecular directions and molecular velocities in the effusion beam, and the upper pressure limit at which the method is suitable. Many of these problems have been discussed previously (84 to 88). Carlson (89) has

studied some of these problems both theoretically and experimentally. The theoretical investigation yielded expressions for the frequency of molecular collision at various points on the walls of a Knudsen cell and for the extent of saturation within the crucible. At pressures varying over a million-fold range he measured the transport of saturated mercury vapor from an isothermal crucible fitted first with a thin-edged orifice and then with long narrow channels. The thin-edged orifice measurements showed the transition from molecular to hydrodynamic flow. Experiments with the long channels revealed: the transport at low pressures is given by the Knudsen long-tube formula; Knudsen's minimum existed; viscous flow becomes important at higher pressures; and, in the neighborhood of one atmosphere, the flow approaches the limiting value which would be expected if the channel were saturated with vapor. Some of the results give an insight into the upper pressure limit for the Knudsen method. Phipps and his students (90a to 90d) have continued their studies of the distribution of molecular directions from effusion chambers.

Vaporization and condensation.—Hirth & Pound (91) have extended an earlier theoretical development of the coefficients of vaporization and condensation. They now include the effect of surface diffusion and point out that the vaporization coefficient and the condensation coefficient, usually assumed to be the same, can be identical only in very rare circumstances unless the two coefficients are equal to unity. Ritger (92) has discussed theoretically the rate of establishment of equilibrium in a liquid-vapor system, and Zwick (93) has also investigated theoretically the vaporization coefficient as a function of the velocity of the vapor relative to the interface.

Miscellaneous.—Boerdijk (94) has discussed the theory of a general thermocouple and has described its relationship to heating and cooling.

The activity of an intermediate phase in a chemical system is ordinarily taken as unity by chemists, but this choice is not convenient if wide solid solution exists in the system. Searcy (95) has discussed using the free energy of formation per gram atom of component element rather than the free energy of formation per mole of compound. In general terms, Brewer (96) has described the important thermodynamic considerations in connection with new high temperature species.

TEMPERATURE MEASUREMENT

Textbook chapters on temperature measurement have been written by Margrave (97) and Kingery (7). Lier (61) has compiled a bibliography on temperature measurement. At a conference on the pyrometric temperature scale, Kostkowski [see (72)] reviewed the international temperature scale and various instruments for achieving it above 1000°K., and pointed out the accuracy and precision of such temperature measurements.

It was stated at this conference (72) that a comparison of tungsten strip lamps made in 1957 and 1958 showed that the temperature scales between 1063 and 2200°C. in the national standards laboratories in Germany, Eng-

land, Canada, and the United States were in agreement. It should be realized, however, that occasional incorrect calibrations may occur through human or instrument error; therefore, single calibrations of great importance should be viewed cautiously. Two or more instruments calibrated at different times should be intercompared to reduce the probability of error.

Thermocouples.—Roeser & Lonberger (98) have described methods for testing and calibrating thermocouples and thermocouple materials in an U.S.NBS circular that should prove to be the standard reference source on such topics.

The desirability of thermocouples suitable for temperatures above platinum-platinum/rhodium has long been recognized. There have been significant developments using rhenium tungsten alloys and rhodium iridium alloys. Sims, Gaines & Jaffee (99), Davies (100), Rudnitskii & Tyurin (101), and Hurd (102) have described the thermoelectric properties and stability of tungsten rhenium thermocouples that should be suitable to about 3000°C. Lachman & Kuether (103) have discussed the stability and reliability of tungsten-rhenium thermocouples and rhodium-iridium thermocouples. It is to be hoped that developmental work on these new thermocouple materials will continue, and that the Bureau of Standards will undertake an investigation of their properties when additional work is done.

Optical pyrometry.—In a paper of great importance to optical pyrometry, Russell & Schofield (104) discuss the mathematical theory of the tungsten lamp. Such lamps are used in disappearing-filament optical pyrometers and as secondary temperature standards. Assuming that the resistivity and emissivity of tungsten vary directly as the temperature, and that the thermal conductivity remains constant, they derived equations for the temperature distribution along an electrically heated wire or strip. Not only did they calculate the voltage on, the resistance of, and the temperature distribution along a filament of known dimensions when it was carrying a constant current with its leads at a constant temperature, but they also calculated the effects of temperature gradients in the leads, the effects caused by the Peltier and Thomson effects, and the so-called temperature coefficient of calibration, that is, the change of the temperature of the filament with the change of the temperature of the surroundings. They discussed both the steady state temperature distribution and the rate at which the filament can be expected to achieve its final temperature. They compared their calculated results with measurements on typical lamps and found excellent agreement. They even went so far as to make suggestions for modifications on the design of strip lamps commonly used for optical pyrometer calibrations. It is to be hoped that their work will encourage manufacturers, calibrators, and users to improve their techniques.

The spectral emissivity and total emissivity of molybdenum, tantalum, and tungsten have been measured with a new technique by Allen, Glasier & Jordan (105). The method employs the measurement of the brightness temperature at the center of a heated rod as a function of the heat flow, and pre-

sumably allows the measurement of the emissivity to be made without the necessity of producing a blackbody. The results can be compared directly with those of many earlier investigations, but they do not mention the tabulation of spectral emissivities for tungsten by Forsythe & Adams (106) nor the relatively recent work of De Vos (107). Inasmuch as their results are roughly 15 per cent lower than the earlier work that they do not mention, their work should be re-examined.

In an earlier paper, Lovejoy (108) has discussed the accuracy of optical pyrometers in the 800–4000°C. range. He has discussed the extension of the range (109) of optical pyrometry to temperatures below 800°C. by removing the red filter and finds standard deviations of about six degrees at 600°C. He suggests that this technique may be useful in some types of experiments not requiring great temperature precision. He also has discussed (110) the extension of the optical pyrometer range to temperatures up to 8000°K. and has pointed out that absorbing filters can be used satisfactorily to cover this range if certain precautions are taken. In this last paper he presented a review of the general theory of optical pyrometry.

Other developments.—There are several studies underway to take the human eye out of pyrometry. Studies on photoelectric pyrometers were reported by Bowman and by Johnson & Erminy [see (72)]. It is reasonable to expect that within the foreseeable future such instruments will replace the ordinary optical pyrometer for very precise work. The latter is, however, a very convenient and precise instrument, and its early demise is not envisioned. Blum (111) has described a recording optical pyrometer for use in the temperature range between 1300–3000°C., with a reliability of $\pm 20^\circ\text{C.}$ and a time constant of a few milliseconds. It is thought to be suitable for measuring transient high temperatures.

Temperature measurement by radiation pyrometry as distinct from optical pyrometry is discussed in a book by Harrison (112).

TECHNIQUES AND APPARATUS

Excellent descriptions of experimental methods and techniques for equilibrium studies at high temperatures have been written by Kingery (7), Chipman, Elliott & Averbach (113), Richardson & Alcock (114), and Margrave (115).

Mass spectrometry.—The most spectacular results in high temperature chemistry during the past few years have come from the mass spectrometer. Inghram & Drowart (116) have given an excellent discussion of mass spectrometry and its applications to high temperature chemistry. They list the advantages and possibilities for the instrument, describe the various components and procedures, and present a very valuable tabulation of over a hundred vaporization reactions studied mass spectrometrically.

Probably the largest source of error in thermodynamic measurements with a mass spectrometer arises from errors in the temperatures, which are frequently measured by means of an optical pyrometer. It is not always possible

to obtain good blackbody conditions or to make appropriate emissivity corrections. Temperature gradients within the cell may be hard to detect, and, furthermore, would influence the proportions of species emerging from the hole.

Although most of the systems have been studied with a single focusing, magnetic-field mass spectrometer, and while this kind of instrument is still the most popular, some recent work has utilized a time-of-flight mass spectrometer. For example, Cater, with Thorn and Rauh (117), Milne & Klein (118), and White and co-workers (119) have studied the evaporation of US and UOS, the alkali halides, and the rare earth metals, respectively.

A recent innovation in mass spectrometric technique involves the reaction between a solid sample contained in a Knudsen cell and a gas that comes from an external gas handling system or from an attached Knudsen cell (120, 121, 122). The gas can be admitted at any pressure by altering conditions in the external system or by varying the temperature of the attached cell. Another technique in mass spectrometry involves the use of two filaments for the study of reflection of atoms from a hot surface. Chupka (123) has used this technique for some preliminary studies on graphite. Searcy, Williams & Schissel (124) have suggested the use of constant boiling systems for calibration of mass spectrometers.

Waldron (62) has edited the proceedings of the mass spectrometry conference held in London in September, 1958. A bibliography containing papers on mass spectrometry is given. Particular papers of interest are those by Frost & McDowell (125) on electron impact studies and by Goldfinger & Jeunehomme (126) on studies of compounds from elements on opposite sides of group IV and also on the elements of groups V and VI.

The transpiration method.—Richardson & Alcock (114) and Margrave (115) have discussed the principles of the transpiration or entrainment method, which is one of the most satisfactory ways of measuring vapor pressures and dissociation pressures. In its simplest form the method consists of measuring the transport of evaporated material carried by an inert gas passing over the evaporating sample. If the flow rate is too great the carrying gas will not be saturated, and the apparent vapor pressure will be too low. It has been customary to make measurements at several flow rates and to extrapolate to zero rate to eliminate the effect of lack of saturation. Such an extrapolation procedure is unwarranted, and it may lead to large errors because diffusion occurs if the rate of flow is too slow, and the apparent pressures will be too high. Merten (127) discussed the problem and derived the equation

$$P = \frac{m}{tv} \frac{RT}{M} \left[1 - \exp \left(- \frac{vl}{DA} \right) \right] \quad 1.$$

in which P is the pressure, R , T , and M have their usual significance, m/t is the mass transported per unit time, v is the volume passed per unit time, l is the length of the capillary downstream, D is the diffusion coefficient of the vapor, and A is the cross sectional area of the capillary. For large values of v

the diffusion effects are negligible and the pressure assumes the usual, simple value $(m/v)(RT/M)$, but at small values of v the diffusion flow becomes important and P becomes $(m/l) (RT/M) [(DA/1) + v/2]^{-1}$. He has pointed out that the equations may be used to obtain not only the pressure but also the diffusion coefficient in favorable instances. Recent results by Ackermann *et al.* (128) and data cited by Richardson & Alcock (114) show the kind of behavior predicted by the equation.

The torsion method.—Because of the speed with which vapor pressure measurements can be made and the possibility of directly measuring molecular weights of effusing vapor, the torsion effusion method has been receiving considerable attention. In this method the sample is placed in an effusion cell suspended by a torsion fibre. The cell contains two holes on opposite sides, displaced in opposite directions from the center. Vapor effusing through the holes causes a torque to be exerted on the cell and the rotational displacement of the cell can be measured by a mirror attached to the suspension. Vapor pressure studies using this method include Barrow *et al.* (129) on zinc, Pugh & Barrow (130) on alkali metal halides, Witt & Barrow (131) on AlF over $Al-AlF_3$, Aldred, Filby & Pratt (132) on cadmium and alloys, Scheer on B_2O_3 (133) and B_2O_2 above $B-B_2O_3$ (134), Meschi & Searcy (135) on Al_4C_3 , Sime & Gregory on $CrBr_2$ (136) and on the iron halides (137), and Hildenbrand (50) on alkali and alkaline earth halides. Vapor pressure measurements performed by this technique can be accomplished in a few minutes and appear to be in reasonable agreement with those obtained from other experiments. Sime and Gregory did note, however, that results obtained on $FeBr_2$ and FeI_2 with two different cells did not give the same values, and neither set was in agreement with ordinary effusion measurements. They attributed the discrepancies to vaporization coefficient effects. Improvements in the method have been suggested by Rosen (138) and by Freeman (139) who have designed null point torsion effusion equipment.

Despite the agreement between pressures obtained by this method and those obtained by other methods, the molecular weight results are disappointing. Molecular weights can be calculated because the torsion measurement gives the pressure directly, and the effusion method gives the $P\sqrt{M}$. Scheer (133, 134) apparently has been successful in obtaining molecular weights. Not many other attempts have been made, but Hildenbrand's results apparently give low molecular weight values when compared with mass spectrometric results. He has pointed out that Searcy & Freeman (140, 141) also obtained low values for tin and germanium.

The ease, rapidity, simplicity, and low cost of this technique, especially in comparison with that of a mass spectrometer, make the method very attractive, and every effort should be expended to refine it.

Several difficulties can be cited. If induction heating is to be used, the crucible must be shielded by a sufficiently large susceptor so that additional deflections or oscillations are not introduced into the torsion system. Both the absolute pressure determination and the weight loss determination enter

as their squares in the calculation of the molecular weight, and their errors are therefore doubled. The pressure is a sensitive exponential function of the temperature, and it is difficult to perform both experiments under suitably controlled conditions so that the temperatures can be precisely related to each other. To eliminate this difficulty, one can perform both parts of the experiments simultaneously, but if this procedure is followed the speed of the torsion method is lost. Finally, appropriate but different orifice corrections must be made in the two parts of the experiment. Clausing (84) has calculated the orifice corrections for total flow, and Freeman & Searcy (88) have calculated them for the pressure experiment. It has never been demonstrated that either treatment accurately describes the actual situation. These orifice corrections may well be the source of the difficulty with the method. The work already mentioned by Carlson (89) and others appears to be a step toward solving some of these problems.

Molecular beams.—Molecular beam studies are of considerable importance because they have been used to obtain the velocity distribution of molecules effusing from an oven which in turn is useful for obtaining fundamental information about the effusion method and for establishing the proportion of polymers in vapors. They have also been used to study intermolecular reactions in the gas phase, and the interaction of gases with surfaces. Various molecular beam papers dedicated to Otto Stern have appeared in a book edited by Estermann (142). Many of these studies employ a rotating mechanical velocity selector to measure the velocity distribution in the beam. Hostettler & Bernstein (143) have designed a new one consisting of six slotted discs.

Marcus & McFee (144, 145) studied the velocity distribution of potassium atoms effusing from the oven and found that at low pressures the beam is essentially Maxwellian, but at high pressures there is a deficiency of low velocity atoms. With the beam whose properties they had just studied as a source, they used the selector to measure the velocity distribution of atoms reflected from solid surfaces. The temperatures of the reflected beams corresponded closely to the temperatures of the reflecting surfaces except in the case of a cleaved LiF surface. In this instance, the energy of exchange between the beam and the surface was found to be only about 70 per cent of the maximum possible when the surface was between 600 and 900°K.

Hurlbut (146) has studied molecular scattering at solid surfaces in order to obtain the microscopic picture of momentum and energy exchange between the directed particle and the surface. His results show that, for air, nitrogen, argon, and for a glass surface, by far the greatest number of molecules were scattered at random. There was, however, a small departure from this cosine scattering in some cases. Datz & Taylor (147), in reporting on applications of molecular beam techniques to chemistry, have described gas-surface interactions, surface ionization, and gas-gas interactions.

Other techniques.—Cater, Plante & Gilles (148) devised a new technique

for high temperature chemistry that employs a closed crucible, and applied the technique to a study of the tantalum and molybdenum oxides. They point out that such a technique can be used to measure the reaction between a sample and its crucible under conditions such that evaporation loss is unimportant; to establish the loss of sample through the crucible walls; to approximate diffusion coefficients; to measure the composition of vapor leaving the crucible walls after leakage; to identify migrating species; to indicate the existence of two or more important gaseous species in an evaporating system; to obtain thermodynamic information; and to obtain crystals for x-ray diffraction investigation.

It has been recognized for a long time that the electron diffraction technique should be useful for establishing molecular structures in high temperature systems. Akishin and co-workers have used this technique for the gaseous Ga, Y, La, and Nd halides (149), for B_2O_3 (150), and for Li_2O (151). Bauer, Ino & Porter (152) have used an instrument to establish the molecular structure for Li_2Cl_2 . The technique is also useful for the study of crystal structure in films, and Beletskii & Erusalimskii (153), for example, have studied the neodymium oxides.

Brenden, Newkirk & Bates (154) have discussed the principles of microscopy above $750^\circ C$. Nedumov (155) has designed and used a high temperature, non-contact method for thermal analysis.

VAPORIZATION PROCESSES

The study of a vaporization process serves to establish the nature and energetics of chemical binding in the gaseous state; to establish the nature of high temperature reactions; to measure the thermodynamic properties of solids, liquids, and gases; to study the kinetics of high temperature reactions; and to prepare new substances. Many of the facts required for the testing of chemical binding theories come from high temperature vaporization studies.

Usually the study of a vaporization process proceeds through five consecutive stages: (a) the net reaction is established, (b) the gaseous species are identified, (c) the vapor pressure is measured, (d) the kinetics of the evaporation process may be measured, and (e) finally the detailed mechanism of the vaporization process can be established. Sometimes the chronological order of (b) and (c) are reversed. Most of our present studies in connection with vaporization processes are in the first three stages.

Vaporization processes are chemical reactions for which net reactions always can, and should, be written. The equations must specify the state of the substances involved, take into account the phases present in the system, and be consistent with the phase law. Solid solutions are important in many high temperature systems and must be recognized and properly handled.

One-component systems are simple from the thermodynamic point of view since, when both a condensed phase and a gas phase are in equilibrium, there is one degree of freedom and the pressure depends on the temperature

alone. Many one-component systems are complicated because of the existence of polymers in the gas state, but for each constituent the pressure depends only on the temperature.

In two-component systems three cases are of interest: those with a gas phase and either one, two, or three condensed phases. Because of extensive solid solubility, many vaporizing systems contain only one condensed phase and have two degrees of freedom, ordinarily taken to be the temperature and the composition of the condensed phase. If these are specified, the composition of the gas phase and the pressure are fixed. In the titanium oxygen system, for example, there is very wide solid solubility around TiO. The predominant gaseous species are $\text{TiO}(g)$ and $\text{Ti}(g)$, and the proper equations to write for the evaporation from the solid solution are,



The quantity x is the composition variable in the solid phase. Equilibrium can be established in the gas phase according to the reaction.



If these three are taken as independent reactions, the evaporation of oxygen from the solid solution is not independent, and we can regard reactions 2 and 3 as the important independent vaporization reactions. Whenever the temperature and x are fixed, the pressures of Ti, TiO, and O are all fixed, and, therefore, the total pressure and the composition of the gas phase are fixed. If x changes, the pressures and the gas composition change. In this system the evaporation of the solid solution is incongruent, i.e., the composition of vapor phase is different from that of the condensed phase. It is not appropriate to write the reaction

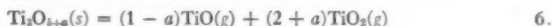


because it demands (a) that the compositions of vapor and solid be identical and (b) that the process be congruent, and neither condition is attained.

The incongruence of the process causes the solid composition to change as vapor is removed, and an attempt to measure the pressure by a Knudsen technique would be inappropriate because of a continual change in x . It has been pointed out (116) that one big advantage of the mass spectrometric method of measuring pressures is that only a small portion of the sample is vaporized, so the composition of the solid remains essentially constant. It should be realized that the properties of TiO in TiO_x will be different from the properties of stoichiometric $\text{TiO}(s)$, and one cannot get precise thermodynamic information on gases from vaporization reactions themselves unless precise data are available for the condensed composition being studied. Reactions involving only gases that may arise in a vaporizing system may be studied mass spectrometrically to give thermodynamic data without data for the condensed phase.

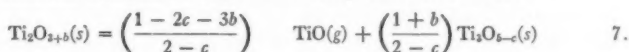
In the case of a congruently evaporating phase, only one degree of free-

dom exists because of the restriction that the composition of the two phases is the same. It has been shown (156) that the congruently evaporating composition in the titanium oxygen system lies within the Ti_2O_3 solid solution region. If the major gaseous species produced by the vaporization are TiO and TiO_2 , the appropriate reaction is



in which a is zero only if stoichiometric Ti_2O_3 is the congruently evaporating composition. In this instance, a is fixed; the composition of the gas phase is the same as that of the condensed phase; we have a congruent process; and at constant temperature the pressure is fixed. At any other composition in the Ti_2O_3 region, the same considerations as were discussed for TiO will apply.

The next case, in which there are two condensed phases, is simpler because there is only one degree of freedom, and when the temperature is fixed the pressure and the composition of all the phases are fixed. For example, in the region between Ti_2O_3 and Ti_3O_5 the most important reaction is



in which b and c give the compositions of the oxygen-saturated Ti_2O_3 and the titanium-saturated Ti_3O_5 respectively. If both Ti_2O_3 and Ti_3O_5 are stoichiometric, b and c become zero and the equation is,



A similar equation could be written for the evaporation of titanium from this condensed system. With three phases present, the pressure and the composition of each phase are fixed by the temperature alone. Here again it should be realized that the thermodynamic properties of $\text{Ti}_2\text{O}_{3+b}$ will not be the same for stoichiometric Ti_2O_3 . From an experimental point of view, such a system may be difficult to study owing to a surface impoverishment of Ti_2O_3 . A further complication arises if one attempts to measure thermodynamic properties from temperature coefficients while the composition at the edge of a solid solution region varies with the temperature.

The final example of two-component systems, one in which there are three condensed phases, has no degrees of freedom but is ordinarily unimportant because of the unlikely possibility of choosing a unique temperature that is required.

Considerable attention is now being directed toward three-component systems, which must be recognized as such when they appear. Just as CaCO_3 produces a two component system, a system containing only two ingredients may produce a three component system. For example, a system prepared by mixing MgF_2 and B_2O_3 produces a three component system because of the formation of the gaseous product OBF . For the three-component system the existence of five phases, i.e. one gas phase and four condensed phases, is relatively unimportant because of the small likelihood of the system occur-

ring at the experimental temperature. With one gas and three condensed phases, we have the most convenient system to consider because there is one degree of freedom, and when the temperature is fixed the pressure and compositions of all the phases are fixed. With one gas and two condensed phases, not only must the temperature be fixed but also the composition of one of the phases must be fixed in order for the pressure to be fixed. If there is only one condensed phase, then two composition variables for this phase, as well as the temperature, must be specified in order to fix the pressure.

Elements.—The vaporization processes of graphite have already been discussed (75). Two groups of workers have studied the evaporation of the rare earth elements in mass spectrometers. Using the same magnetic field instrument as did Johnson *et al.* (157) in studying Pr and Nd, Savage, Hudson & Spedding (158) studied Sm, Dy, Tm, and Yb. Working at temperatures about 200° higher, White, Walsh, Goldstein & Dever (119) used a time-of-flight instrument to study Pr, Nd, Gd, Tb, Dy, Ho, Er, and Lu. Direct comparisons can be made between the two groups in three instances: Pr, Nd, and Dy. The agreement is not satisfactory. The results of White and co-workers are lower by 7.6 kcal. for praseodymium and by 9.8 kcal. for dysprosium and higher by 2.2 for neodymium. The results of Spedding and co-workers are in very good agreement with results obtained by Spedding and other co-workers by different techniques (159, 160), and the results of White and co-workers are said to be in better accord with studies by White and other co-workers in their studies of Dy_2O_3 (161). It is possible that the discrepancies between the two groups of workers are caused by different temperature scales or by temperature gradients in their crucibles. Despite these disagreements, both groups demonstrate enormous differences among the vapor pressures of the rare earth elements.

Oxides.—Ackermann & Thorn (162) have written a critical review of the vaporization reactions of the oxides, and only a few systems will be discussed here. Stimulated by the problems arising in the burning of boron fuels, about six different groups have been involved in the study of the boron oxygen system. Evans, Prosen & Wagman (163) have tabulated heats of formation and thermodynamic functions for boron and some of its compounds. It has been known for some time that B_2O_3 evaporates to form $B_2O_3(g)$ under neutral or oxidizing conditions. Under reducing conditions, however, $B_2O_2(g)$ is produced. White, Walsh & Rentzepis (164) recently measured the $B_2O_2(g)$ pressure above B_2O_3 in graphite and obtained a slightly different value for its heat of formation.

White, Mann, Walsh & Sommer (165) studied the infrared emission spectra of $B_2O_3(g)$ and $B_2O_2(g)$ and deduced a "V" structure with C_{2v} symmetry for $B_2O_3(g)$. Akishin & Spiridonov (150) have studied gaseous B_2O_3 in an electron diffraction apparatus and have obtained a BOB angle of 95 degrees instead of 120 degrees.

The boron sulfur system is similar to the boron oxygen system, and Greene & Margrave (166) and Sommer, Walsh & White (167) have studied

the gaseous boron sulfides with infrared spectrometers. The latter workers have also identified some of the species in a mass spectrometer and have proposed some bond energies.

The aluminum oxygen system has been the subject of considerable study and controversy for a number of years. Sears & Navias (168), De Maria, Drowart & Inghram (169), and Drowart, De Maria, Burns & Inghram (170) have studied the system. The last group report mass spectrometric measurements for the vaporization of Al_2O_3 from tungsten and from molybdenum Knudsen cells. They state that reaction between Al_2O_3 and tungsten gives pressures of WO_2 , AlO , and Al_2O_2 about one-tenth the pressures of atoms. They point out discrepancies between earlier work and theirs, and it seems safe to say that the last word has not yet been written about this system. Reduction of Al_2O_3 by molybdenum seems to occur in the condensed phase, and accordingly this system is more complicated.

Walsh, Goldstein & White (161) have found the predominant species above rare earth sesquioxides to be O(g) and MO(g) , for which they have reported dissociation energies. Schick (171) has reviewed the vaporization studies on SiO_2 and has collected the results in equations and plots. Under neutral conditions, SiO_2 vaporizes predominantly to give SiO and $\frac{1}{2} \text{O}_2$ at all temperatures. The ratio of the pressures of SiO to SiO_2 is about 30 at 2000°K . and about 10 at 3000°K . The boiling point is $3070 \pm 75^\circ\text{K}$. In oxidizing conditions the vaporization of SiO(g) is inhibited, while under an atmosphere of air, SiO(g) and $\text{SiO}_2(\text{g})$ have approximately equal pressures at 2300°K . At higher temperature SiO becomes more important. In a reducing system, SiO(g) will be even more important. Cater, Plante & Gilles (148) and Goldstein, Walsh & White (172) independently observed that a Ta_2O_5 sample heated in a tantalum crucible diffused through the walls to escape from the outside as TaO(g) and $\text{TaO}_2(\text{g})$. The first-mentioned group used the transport from a closed crucible to estimate the proportions of the gases leaving the surface, and the other group suggested that equilibrium involving tantalum oxides and other oxides is not readily established in effusion crucibles.

The gaseous oxides of group VI elements are complex and interesting. The sublimation of MoO_3 has been studied mass spectrometrically by Burns *et al.* (173), in a closed crucible by Cater, Plante & Gilles (148), and in a Knudsen cell by Plante (174). The properties of the molybdenum, tungsten, and uranium oxides have been measured with transpiration techniques by Ackermann *et al.* (128) and mass spectrometrically by De Maria *et al.* (175). Chupka, Berkowitz & Giese (176) have studied mass spectrometrically gaseous tungsten oxides in connection with their work on BeO . The measurements with the mass spectrometer, the closed crucible, and the effusion cell all show good agreement with respect to the thermodynamic quantities deduced. They are in agreement that $\text{MoO}_2(\text{g})$ constitutes about 4 per cent of the vapor in equilibrium with $\text{MoO}_3(\text{s})$ and that the previous work (177) is incorrect. The mass spectrometer results indicate that the most important species above MoO_3 are MoO_3 , Mo_2O_6 , MoO_2 , and Mo_2O_5 with each being

lower than the preceding one by a factor of about four. Ackermann *et al.* (128) have presented their results in the form of free energy equations for the vaporization of the trioxides and U_3O_8 and have discussed the differences among the three systems. De Maria *et al.* (175) and Chupka *et al.* (176) present their results in terms of atomization energies, and they are in good agreement with each other.

Alcock & Hooper (178) and Schäfer & Tebben (179) have measured the transport of platinum in flowing oxygen and have found two oxygen atoms per molecule. The former workers have used various gold-platinum alloys to show one platinum atom per molecule. The results of the two groups are in substantial agreement, and the pressure of PtO_2 in equilibrium with metal in an atmosphere of oxygen is 10^{-5} atm. at about 1650°K. The former workers have also studied the oxides of Rh, Ir, Ru, and Pd. Schäfer & Heitland (180) have studied the iridium-oxygen system. Carpenter & Mair (181) and Clark, Dickinson & Mair (182) have found surface effects to be the major factor in the interaction of oxygen and hot gold. Gaseous molecules were not found.

Ternary systems.—It has been recognized for several years that the volatility of B_2O_3 is considerably greater in the presence of water, thus indicating the presence of a gaseous hydroxide. Greene, Randall & Margrave (183) have discussed the background of this problem; Evans, Prosen & Wagman (163) have summarized some of the earlier work on the system; and Wilkins & Altman (184) have calculated some thermodynamic properties for boron oxygen hydrogen compounds. The gaseous substance, HOBO, that was found by Margrave (185) has been confirmed by Meschi, Chupka & Berkowitz (121), who studied the reaction between B_2O_3 and water in a mass spectrometer. They deduced its heat of formation and found $H_3B_3O_6$ to be present to an extent of less than 1 per cent at temperatures between 1061 and 1451°K. White *et al.* (186) have studied the infrared emission spectrum of HOBO and have found that the H is off the line containing the OBO group.

The vaporization of BeO and its reaction with tungsten have been studied by Chupka, Berkowitz & Giese (176) mass spectrometrically, and by Pollock, Saul & Milne (187) using the Knudsen method. The vapor consists predominantly of atoms and BeO trimer and tetramer with smaller amounts of monomer, dimer, pentamer, and hexamer. In addition, gaseous molecules of the type $WO_x \cdot (BeO)_y$ with $x = 1, 2$ and $y = 1, 2, 3$ were found. The results of the two groups were in agreement.

Other important work on systems containing three elements continues to appear. Berkowitz, Meschi & Chupka (188) have studied the reaction between Li_2O and H_2O . Inghram and co-workers have (189) studied the germanium-silicon-carbon system. Schäfer and his group (190, 191) are continuing the excellent studies on the chlorides and oxychlorides of niobium and tantalum. Difficulties in obtaining reproducible results were experienced by Rao & Schoonmaker (192) in their study of NaOH.

Other work.—There have been two recent studies of vaporization properties of boride systems. Leitnaker (193) has studied the zirconium-boron

system, and Knarr (194) has studied the silicon-boron system. Cater (117) has studied the evaporation properties in the uranium-sulfur system and in the uranium-oxygen-sulfur system. In the former, both $US(g)$ and $U(g) + S(g)$ are important, and in the latter system, $UOS(g)$ was identified. Pollock (195) has studied the vaporization properties of Be_2C . Goldfinger & Jeunehomme (126) and Porter & Spencer (196) have measured with a mass spectrometer the vaporization from various intermetallic systems.

There was other work on various oxides as follows: Be (197), Li (151, 198, 199, 200), Sr (201), Al (202), As_2O_3 evaporation and condensation (203, 204), Te (205), V (206, 207), Cr (208), Fe (209), and a review of several (210).

On sulfides and selenides, work included some on Ca (211), Te (212, 213), Zn (214 to 217), and a review of several (210).

There were several reports of work involving oxides and H_2O . They were for Li (122, 188), Be (218), W (219), and U (220).

Work has continued on the alkali halides (118, 120, 152, 221 to 227), which show monomers, dimers, and trimers in the vapor. Other work on halides has been reported also: alkaline earths (228), group III (229 to 232), Bi (233, 234), Au (235), Cr (136), W (236, 237), Ru (238), Fe (137), the actinides (239), several transition metals (240), and several solid solutions (241).

Vapor pressures were reported for some metallic systems and alloys: Na (242); alkaline earths (243, 244, 245); Al (157); B (246); Ag (247); Cu, Ag, and Au (248); Zn and Cd (249); Cr (250); Mn (247, 251); Pd and Pt (252); Nb (253); and Cu and Ni (245).

There were reports on $ZnAs_2$ (254) and the molybdenum-silicon system (255).

MISCELLANEOUS TOPICS

The chemical analysis of high temperature materials is an extremely difficult field and one in which considerably more effort is needed. Kriege (256) has reported some excellent procedures.

The determination of phase behavior and the crystal structure of systems that are important at high temperatures has continued, but only two areas of activity will be mentioned. The complexity of solid phases and the importance of solid solutions in high temperature work becomes even more significant. Magnéli and his co-workers (257 to 262) have continued their valuable work in determining the crystal structure of important complicated oxide systems. Guinier (263) has discussed heterogeneities in solid solutions and Emeleus & Anderson (264) have discussed some interstitial and non-stoichiometric compounds.

Practical developments utilizing many of the results of high temperature studies are now appearing. A large number of these are in the field of nuclear energy. Power reactors are summarized by the Atomic Energy Commission (265); nuclear rockets are discussed by Newgard & Levoy (266); plasma thermocouples are discussed by Pidd (267), Grover (268), and Bowman

(269); and several pyrometallurgical processes are discussed in the journal by that name.

There has been a large number of reports concerning materials for high temperature uses. Bradshaw & Matthews (270) have collected the properties of refractory materials. Ackermann & Thorn (271) have reviewed the free energies, entropies, and enthalpies of formation for elements, solid carbides, and gaseous oxides. Livey & Murray (272) have discussed the stability of refractory materials. Mackenzie (273) has tabulated container materials for various melts and has presented a method for testing refractory suitability. Discussions have appeared on refractory metals by Campbell (274), high temperature alloys by Cieslicki (275), cermets, intermetallics, and refractory metals by Hehemann & Ault (66), nuclear materials by Beard (276), reactor materials in the book edited by Tipton (17), and borides by Aronsson (35) and Steinitz (36). At the International Symposium on High Temperature Technology, refractory metals (277), oxides for high temperature applications (278), graphite and carbide, nitride and sulfide refractories (279), silicides, borides, aluminides, intermetallics, and other unique refractories (280), and materials and techniques for thermal transfer and accommodation (281) were discussed. Lang (282) has announced the establishment of a "bank" of high temperature ceramics and cermets and has reported some of the properties for these specimens.

The Materials Advisory Board, the National Academy of Sciences, National Research Council has published a report on plasmas and related high temperature devices (283).

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ION EXCHANGE¹

BY ROBERT KUNIN

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Although over 1000 articles on ion exchange appear annually in the technical literature, the major portion of these refer to industrial and analytical applications of ion exchange materials. Only a few articles have appeared during the past year which have improved our basic understanding of ion exchange from a rigorous physical chemical point of view. There are several inherent difficulties, which are often neglected, in applying standard physical chemical practices to the study of ion exchange systems; i.e., (a) inability to measure directly phenomena occurring within the exchanger phase, (b) heterogeneity of the exchanger, and (c) high electrolyte concentration of the exchanger phase. The fact that most ion exchange systems involve a heterogeneous system, solid-liquid, in which the solid phase is an extremely concentrated solution of a cross-linked polyelectrolyte, is a huge obstacle to the physical chemist. The physical chemistry of dilute solutions of uncross-linked polyelectrolytes must be solved before a clear understanding of the much more complicated cross-linked polyelectrolytes, the ion exchange resins, can be properly attacked by the physical chemist.

Several books and reviews on ion exchange have been published during the past year. The contributions of interest to the physical chemist are those of Salmon & Hale (1a), Kunin (1b), and Helfferich (1c). The status of ion exchange in the U.S.S.R. has been summarized in a book edited by Chmutov (1d) and a summary of ion exchange in Communist China has been summarized by Ping-Lin Ho (1e). From an overall point of view, the efforts of Red China are considerably behind those of the U. S.; however, the status of ion exchange in the U.S.S.R. is on a high level. Of considerable interest is the summation in the Seventh Edition of the Merck Index (1f) on the basic properties of the many ion exchange materials available throughout the world.

THE STRUCTURE OF ION EXCHANGERS

Some concerted effort has been directed towards an understanding of the internal structure of ion exchange materials, with particular attention being given to the ion exchange resins. The structures of the crystalline zeolites, or the "molecular sieves" as they are commonly called, pose no major problems since their structures can be determined by x-ray analysis and gas adsorption

¹ The survey of literature pertaining to this review was concluded December 1, 1960.

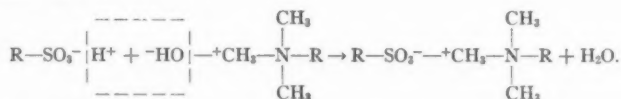
techniques. The amorphous ion exchange resins, on the other hand, pose many problems.

Högfeldt (1g), on the basis of equilibrium studies, finds that considerable heterogeneity exists between the individual beads of a single sample of an ion exchange resin. On the other hand, Suryaraman & Walton (2) using a density gradient technique claim that such heterogeneity does not exist. Therefore, these studies contradict each other, since each investigator employed different techniques and was measuring heterogeneity indirectly; further studies aimed specifically at this problem are indicated. The writer, on the basis of dye studies with various ion exchangers under the microscope, must agree with Högfeldt concerning the existence of some heterogeneity in commercial ion exchangers.

Several studies have been aimed at an analysis of the internal structure of ion exchange resins. Tager (3) suggests that the concept of porosity or microporosity is only applicable to solid, rigid adsorbents, and that these terms cannot be applied to cross-linked ion exchange resins since they are void of permanent pores. Grubhofer (4) proposes a model for the molecular structure of a cross-linked styrene divinylbenzene exchanger in which he attempts a calculation on the distances between polymer chains based upon limiting ion diffusional rates. An insight into the physical structure of carboxylic cation exchangers may be gleaned from the studies of Savitskaya, Yakhontova & Bruns (5) on the limiting capacity for large organic cations.

Further studies on the internal structure of ion exchange resins have been based on the swelling characteristics of resins during the exchange process. Chzi-syan, Savitskaya & Bruns (6), Blasius & Pittack (7), and Lapanje & Dolar (8) have completed several such studies relating the swelling characteristics to the kinetics and ionic screening effects. Of considerable importance are the studies of Kuhn *et al.* (9) on the transformation of chemical energy into mechanical energy during the reversible contraction and elongation of a homogeneous cation exchange system.

Grubhofer (10) has found that oppositely charged ion exchange resins (anion and cation exchangers) adhere to each other because of mutual surface interaction. This results in a low packing factor. The interaction may be expressed as



Of considerable importance to the overall understanding of ion exchange are the studies on well-defined soluble polyelectrolytes. The work of Nagasawa & Rice (11) on the titration curves of maleic anhydride vinylpyrrolidone copolymers indicates that the mean electrostatic field acting on a fixed

charge is dependent upon both the overall charge distribution and the nearest neighbor charge.

ION EXCHANGE EQUILIBRIA

Various thermodynamic measurements have been reported on a variety of ion exchange resins. Dickel *et al.* (12, 13), in a series of isopiestic and calorimetric measurements on a series of cation exchangers of varying skeletal structure and functional groups, found the enthalpy to vary with cross-linkage and observed characteristic "steps" on the uptake of each mole of H_2O per ion. The values differed for each skeletal structure and functional group. Calorimetric studies by Dolar & Močnik (14) indicate that the evolved heat depends largely on the water content and ionic state of the resin and but slightly on the degree of cross-linking.

A number of papers have appeared on the effect of temperature on ion exchange equilibria. These include studies by Matorina & Popov (15), Aleksandrova & Elovich (16), Kraus & Raridon (17), Kraus *et al.* (18), and Bonner & Pruett (19, 20). The work of Kraus *et al.* and Kraus & Raridon was conducted on both anion and cation exchangers at temperatures as high as 200°C. Since the resins are unstable at this temperature the significance of some of their data is questionable. Basically, the changes in ion exchange equilibrium behavior are a reflection of changes in the activity coefficients of the ionic species involved.

Lindenbaum, Jumper & Boyd (21) have studied the effect of exchange capacity on the selectivity coefficient with a series of sulfonic acid cation exchangers and quaternary ammonium anion exchangers of variable capacity. They have concluded that the behavior does not agree with the recent statistical theory; i.e., that increased exchange capacity increases selectivity. For cation exchangers, Kennedy & Wheeler (22) have concluded that selectivity is more dependent upon permanent dipoles than upon the polarizability.

Studies on the ion exchange behavior of anionic metallic complexes in hydrochloric acid solutions at various ionic strengths have been made by Marcus (21a), Marcus & Coryell (22a), Kraus *et al.* (23), and Chu & Diamond (24). However, an explanation for the unusual behavior of these complexes is still lacking.

StreLOW (25) has compiled a most useful table summarizing the distribution coefficients of 43 cations in hydrochloric acid of varying normality for a standard sulfonic acid cation exchange resin. Nelson, Rush & Kraus (26) have summarized the selectivity of a quaternary ammonium anion exchanger for the anionic complexes of nineteen elements (Groups II, III, IV, and V) in mixed HCl-HF solutions. Freeman (27) has found that analytically measured distribution coefficients are subject to experimental error due to imperfections within the exchange resins and that, since these errors are consistent, they may be eliminated.

KINETICS OF ION EXCHANGE

Many of the studies on the kinetics of ion exchange revolve around the diffusion of ions within the particle or through the Nernst film about the particle. Lagos & Kitchener (28) and Fedoseyeva, Cherneva & Tunitskiy (29) have studied the self-diffusion of cations in sulfonic acid cation exchangers in membrane form and have concluded that the influence of cross-linking on diffusion is largely controlled by the water content of the resin. Whereas the resistance offered by the resin network is a major factor, the size and hydration of the diffusing ions and the electrostatic field of the polyelectrolyte structure are also of major importance. Studies by Gerasimov *et al.* (30), Savitskaya *et al.* (31), and Shostenko (32) on the adsorption of dyes, antibiotics, and other large organic cations have indicated that particle diffusion controls the kinetics; however, changes (volume changes, moisture variation, etc.) within the structure of the particle also influence the kinetics.

Some kinetic studies on anion exchangers were reported by Shulka & Bhatnagar (33) and Nelson (34). In the latter study, diffusion in the resin was compared with diffusion in a quaternary amine solution.

Fixed-bed kinetic studies include those of Tien & Thodos (34a, 35) based on linear equilibrium isotherms and those of Tien (36) and Plesset, Helfferich & Franklin (37) on non-linear isotherms. The latter are of interest because of their application to solid diffusion kinetics.

ION EXCHANGE IN NON-AQUEOUS SYSTEMS

Studies on the phenomena of ion exchange in non-aqueous media and mixed solvents have been conducted by Davies & Owen (38), Gable & Strobel (39), and Goenvet (40). Kennedy & Davis (41) have found that LiCl, CuCl, and $\text{Ni}(\text{NO}_3)_2$ can be adsorbed from organic solvents by tertiary amine anion exchange resins through complex formation. Kojima (42) has shown that the distribution coefficients for the adsorption of the Cu(II), Fe(III), and the Co(II) anionic complexes by quaternary ammonium anion exchangers in HCl-methanol solutions increased with increasing concentrations of methanol. Ogawa & Tsujii (43) found similar results for the exchange of the halides.

INORGANIC ION EXCHANGE SYSTEMS

Increased interest in the "molecular sieves" and the use of ion exchange systems at elevated temperatures has stimulated further studies on inorganic ion exchange systems. Amphlett (44) and Frysinger & Thomas (45) have studied the exchange characteristics of clay minerals for cesium, strontium, and yttrium. Self-diffusion of the alkali ions in the zeolite, analcite, was investigated by Barrer & Rees (46, 47). The Sr^{++} - Ca^{++} and F^- - OH^- exchange in the mineral, hydroxyapatite, was studied by Collin (48) and Knappwost (49). Investigations on the exchange characteristics of heteropolyacid salts

and zirconium compounds were reported by Smit *et al.* (50) and Bresler *et al.* (51).

SEPARATION OF ISOTOPES

Although separation of isotopes by ion exchange is not a practical procedure, except perhaps for the nitrogen isotopes, such studies have been helpful for the test of chromatographic theory. Glueckauf (52) has found that the data of Lee & Begun (53) and Lee (54) on the separation of the Li^6 and Li^7 isotopes on a sulfonic acid cation exchange resin are in close accord with theory based upon the Pauling radii for the ions. Panchenkov *et al.* (55), Ohtaki *et al.* (56), and Kakihana (57) have studied the separation of the lithium, sodium, and the nitrogen (NH_4^+) isotopes on cation exchangers in mixed solvents. Yoneda *et al.* (58) have separated the boron isotopes as the borates on an anion exchanger.

ION EXCHANGE CHROMATOGRAPHIC THEORY

Goldstein & Murray (59) have developed the mathematics of ion exchange chromatography from the points of view of (a) general entry, (b) kinetic theory, and (c) equilibrium theory. O'Sullivan (60) has presented a theoretical discussion on gradient elution. Studies on salting-out and solubilization chromatography have been described by Breyer & Rieman (61) and Sherma & Rieman (62).

MEMBRANE PHENOMENA

Peterson & Gregor (63) suggest a theoretical treatment for the estimation of diffusion coefficients from a consideration of pore diameters, tortuosity factors, and moisture content. Meares *et al.* (64, 65, 66) have applied the Nernst theory and the Spiegler model to membrane phenomena (permeability, conductance, etc.). McClintock, Neihof & Sollner (67) have measured the relative rates of electro-migration of different ions of similar charge and have related these values to the polarization. Kressman & Tye (68) have presented a theory relating transport numbers to concentration. Jarvis & Tye (69) have developed an expression for the transport of non-electrolytes during electro-dialysis. The effect of hydraulic pressure on the membrane potential has been studied by Ishibashi & Hirano (70). Titov (71) and Barrer & James (72) have described the characteristics of various organic and inorganic membranes.

CATALYSIS

Several interesting studies on the catalytic properties of the "molecular sieve" zeolites were reported by Kerr & Johnson (73) and Weisz & Frilette (74). The fact that the salt form of these materials is more active for the cracking of hydrocarbons than the acid form is most unusual.

NEW ION EXCHANGE MATERIALS

Although no new basic developments in the synthesis of ion exchange materials of special interest to the physical chemist appeared during the past year, the availability of Amberlite 200, a new sulfonated styrene divinylbenzene cation exchanger of unusual physical and chemical stability, is of practical interest (75).

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RADIATION CHEMISTRY¹

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INTRODUCTION

Radiation chemistry includes the investigation of all chemical changes induced by the action of high-energy radiations. This review is generally restricted to studies of the action of electron, gamma-, x-, and light-particle radiations on molecular compounds, since this area includes most of the work currently classified as radiation chemistry. In such cases the chemical effects result from a complicated sequence of events that is initiated by electronic excitation of the irradiated molecules. Studies of radiation chemistry can be conveniently divided into two categories: (a) studies of elementary processes and (b) studies of mechanism. Investigations of elementary processes in the action of high-energy radiations are widespread. Ultimately, all such studies will have their place in the elucidation of chemical effects but at the present time radiation chemists have only partially assimilated the available information. The boundaries of this field are nebulous and the material included in this discussion is of necessity chosen somewhat arbitrarily. In the field of mechanism, on the other hand, it is quite easy to select work that belongs to radiation chemistry. Much of this work emphasizes the various sequences of reactions of radicals that can account for observed products and there is relatively little attention given to specific effects of the action of the radiation. It is because of the volume of such work that selection must be made, and the material considered here has been chosen to allow the most unified account possible, based on emphasis of elementary processes.

Recent reviews of radiation chemistry have been presented by Hamill (1) and Pikaev (2), the latter emphasizing Russian work. Books on the radiation chemistry of polymers by Charlesby (3) and the radiation chemistry of organic compounds by Swallow (4) have also appeared. A good review of the physical and chemical basis of mechanisms in radiation biology has been given by Platzman (5). Reports of symposia on bioenergetics and comparative effects of radiations, edited respectively by Augenstein (6) and Burton *et al.* (7) contain much recent work on radiation chemistry. A *Discussion of the Faraday Society* on "Energy Transfer with Special Reference to Biological Systems" (8) also contains material of interest to radiation chemists.

The organization of this article conforms with the author's overall view of the field. The emphasis is on the conceptual framework rather than current activity in the various areas. We have also devoted more attention to the condensed state, particularly the liquid state, than to the gaseous state, because more effects are peculiar to high-energy radiation here. The transition

¹ The survey of literature pertaining to this review was concluded in November 1960.

region between liquids and gases is currently under study, but as yet little has been published (9).

TRACKS OF HIGH-ENERGY CHARGED PARTICLES

It is generally recognized that the initial distribution of the transient intermediates formed in particle tracks has important consequences for radiation chemistry of liquids and solids. Various simplified models have been used for studies of the diffusion-controlled reactions in tracks. Such "models" must be in agreement with the energy loss patterns of the primary particles. In this section we consider track structure and the basis for a model that has been used by the author and others.

The penetration of high-energy particles of low charge in matter has been studied extensively. The report of a recent symposium on this subject has just appeared (10). The basic theory was developed principally by Bohr (11) and Bethe (12), leading to the well-known result that the energy loss per unit path of a particle of charge ze in a gas of atoms of atomic number Z is given by

$$-\frac{dE}{dx} = 2\kappa ZN \ln \frac{2mv^2}{I} \quad 1.$$

where κ is the stopping parameter

$$\kappa = \frac{2\pi z^2 e^4}{mv^2} \quad 2.$$

e, m are the electronic charge and mass, v is the particle velocity, N is the number of atoms per unit volume, and I is the "mean excitation potential."

Equation 1 is valid only for non-relativistic particles with velocity v greater than the classical velocities of the bound electrons. The quantity I determines the penetration of such particles in a given material. Much experimental information is accumulating on values of this quantity for various atoms and it is quite well established that I varies *directly* as the atomic number Z (10). A theoretical expression relates I to the distribution of oscillator strength of an atom,

$$Z \ln I = \sum f_j \ln \epsilon_j + \int f'(\epsilon) \ln \epsilon d\epsilon \quad 3.$$

where f_j is the oscillator strength for the j^{th} discrete transition and $f'(\epsilon)$ is the oscillator strength per unit energy interval in the continuum. The sum extends over all discrete transitions and the integral extends over the continuum.

To a good first approximation the stopping power of any molecular material is determined by the overall atomic composition and, therefore, is almost independent of specific chemical binding of the atoms. This fact is frequently called the "Bragg rule" [see Platzman (14)]. Specific effects of chemical binding, however, have been the subject of experimental and theoretical investigation (15, 16). The approximate independence of stopping

power on chemical binding has been interpreted to mean that the most important primary loss processes occur for energies that are high compared with energies of chemical binding, and, at such excitation energies, it is reasonable to assume that the density of oscillator strength depends only upon atomic composition.

The gross structure of the track of a high-energy particle depends upon the primary loss spectrum. To an approximation we shall consider below, this spectrum is determined by the distribution of oscillator strength in the stopping material. Until recently such distribution was known only for the hydrogen atom (12) and the helium atom (17, 18, 19). Recently, electron impact measurements by Lassette & Silverman have led to estimates of the oscillator strength distribution in O_2 and N_2 (20, 21, 27). It is possible, therefore, to discuss the primary loss spectrum of charged particles in these materials in a more quantitative manner.

It is well known that equal contributions to the stopping power of a material for high-energy particles come from glancing collisions, which have low energy loss per event, and head-on collisions, which have high energy loss per event (20). Bethe (13) gives

$$\sigma_j = \kappa \frac{f_j}{\epsilon_j} \ln \left(\frac{2mv^2}{\epsilon_j} \right) \quad 4.$$

as the approximate cross section for excitation of a discrete level with frequency $\nu_j = \epsilon_j/h$ and oscillator strength f_j by a particle of velocity v . In our designation this excitation resulted from a "glancing" collision. We can also say that the differential cross section of an atom for glancing collisions in the continuum at the energy ϵ is given by

$$d\sigma_\theta(\epsilon) = \kappa \frac{f'(\epsilon)}{\epsilon} \ln \left(\frac{2mv^2}{\epsilon} \right) d\epsilon \quad 5.$$

Although formulas 4 and 5 for "glancing" collisions are only approximately valid, they allow the cross section estimate to be made from the oscillator strength [see Miller (22)].

The differential cross section for the energy loss ϵ in the interval $d\epsilon$ by a free electron in collision with a heavy particle is given by classical considerations as:

$$d\sigma = \kappa \frac{d\epsilon}{\epsilon^3} \quad 6.$$

In accordance with the customary assumptions of dispersion theory we take the number of electrons that receive such losses as equal to the oscillator strength of all transitions with energies less than ϵ . Thus for head-on collisions we get

$$d\sigma_A = n(\epsilon) \kappa \frac{d\epsilon}{\epsilon^3} \quad 7.$$

where

$$n(\epsilon) = \sum f_j + \int f'(\epsilon) d\epsilon \quad 8.$$

It is clear that the total contribution of each of these processes to the stopping power, $-dE/dx$, is the same,

$$-\left(\frac{dE}{dx}\right)_g = -\left(\frac{dE}{dx}\right)_h = N \int \epsilon d\sigma_g(\epsilon) = N \int \epsilon d\sigma_h(\epsilon) = \kappa ZN \ln \frac{2mv^2}{I} \quad 9.$$

and the sum gives the result of Equation 1. On the other hand, the average energy loss in a single event is widely different for the two processes. The glancing collisions have a large cross section for low-energy processes and many such losses occur; the head-on collisions have relatively small cross sections at all energies, but the few primary events that occur account for a large energy loss.

Primary loss spectra for O_2 and N_2 , calculated using Lassettre and Silverman's data, are shown in Figure 1. Here $P(\epsilon)$ is the fraction of losses per unit energy that occur at the energy ϵ . The part of the curve shown is essentially independent of the primary particle velocity. Lassettre and Silverman have emphasized that their estimates of the optical oscillator strengths involve long extrapolations and must be considered as rather uncertain. In addition, the primary loss spectrum obtained using our prescription is not exact. On the other hand, the general features of the track structure obtained are subject to less uncertainty. Along the main track is a pattern of randomly-spaced primary events resulting from the low energy part of the spectrum shown in Figure 1, with $\bar{\epsilon} \approx 40$ ev. The part of the spectrum above this region accounts for approximately half of the energy loss by the primary particle and thus has an average energy loss much higher than 40 ev. The events with higher losses form branch tracks which are broken up into patterns of low energy losses similar, in fact, to the primary particle itself. To a first approximation, therefore, the low energy portion of the spectrum (Figure 1) is also the spectrum expected for spurs.

It should be noted that the part of the primary loss spectrum shown in Figure 1 is due to the valence electrons only. The contribution of the K shells will appear above 30 atomic units for O_2 and above 23 atomic units for N_2 . The total contribution of the K electrons to stopping power in these cases is not very large. Platzman (14) has explicitly considered effects of the K electrons for the stopping of protons in water. He has also considered other effects normally assumed to be small, such as energy loss in nuclear collisions.

An explicit model of a track was introduced by Samuel & Magee (23) for use in radiation chemistry of water. At that time it was recognized that the low energy losses along the track of a fast primary particle formed isolated regions containing radical intermediates (called "spurs") and that the occasional delta rays would form tracks of a similar type. The basis for the assumed loss spectrum was cloud chamber data, and no explicit considera-

tion of the delta rays was made. This model has been called the "string of beads" model of the track and has been widely used. The average "spur" as originally used in water radiolysis contained 2.5 radical pairs. The average energy loss in glancing collisions is calculated for O_2 to be 37 ev and for N_2 , 38 ev. It is fairly certain that any reasonable estimate of this value for H_2O would also be in the vicinity of 40 ev, and the estimated primary radical yield per 100 ev, or G value, would be about 6 (i.e., $2.5 \times 100/40$).

In the form presented, this discussion of track structure only applies to particles at velocities much greater than the orbital velocities of all bound electrons. It is believed, however, that the basic features of the track structure obtained are of quite general validity for particles of high enough velocity that successive low-energy losses can be considered as isolated.

It has been recognized that the low-energy losses provide the measure of

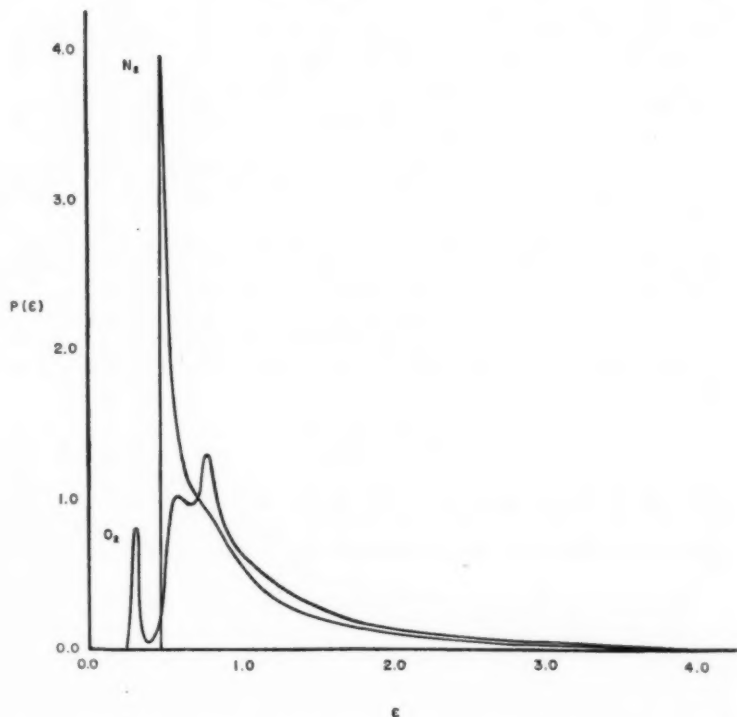


FIG. 1. Primary loss spectra for fast charged particles in O_2 and N_2 . The ordinate is fraction of loss processes per unit energy interval; energy is in atomic units.

the local track effect in radiation action (24). Special considerations of track structures have been made for the purpose of elucidation of chemical action in water by Gray (25) and Burch (26). The former did not introduce an explicit geometrical model of the track, whereas the latter assumed a cylindrical track for all particles.

SPUR STRUCTURE

In the previous section the primary energy-loss spectrum was discussed with little mention of ionization and secondary electrons. Until recently it has been customary to think of primary processes as producing well-defined excitations or ionizations of the constituent molecules, regardless of phase [Fano (28)]. In the past several years it has been realized that cooperative effects occur in condensed phases, and the situation is more complicated than can be described as simply excitation or ionization of single molecules [Fano (29, 30)]. A region in which a low primary energy loss (i.e., below 100 eV) occurs has been called a "spur" in radiation chemistry (23). This designation is completely noncommittal about the response of the matter. However, current interpretations of experimental work require that the principal ultimate effect of the absorption of energy in molecular materials is the formation of radicals. It is also clear that a certain amount of electronic excitation is able to migrate to relatively large distances in condensed phases. We are concerned now with the fate of electronic excitation produced by primary particles.

Let us first consider the nature of the excitation produced by a primary energy loss. It is possible to think of such an excitation as a wave packet formed as a superposition of excited states of the constituent molecules. The uncertainty principle requires that the extent to which such a wave packet can be localized is determined by the de Broglie wavelength associated with the *momentum change* of the particle, $\lambda(\Delta P)$. It is a simple matter to show that

$$\lambda(\Delta P) = \frac{h}{\Delta P} = \frac{h\nu}{\epsilon} \quad 10.$$

where ϵ is the energy loss and ν is the particle velocity. If $\nu \approx 10^{10}$ cm./sec. and $\epsilon \approx 50$ eV, we have $\lambda(\Delta P) \approx 100 \text{ \AA}$, and it is evident that such excitation cannot in any reasonable approximation be considered as localized in a molecule.

There has been little progress in the description of the processes that occur between initial absorption of energy and the formation of the chemical intermediates although the problem has been considered (31). It is clear that if the energy loss is high enough, the excitation essentially amounts to formation of an energetic secondary electron and this is certainly the correct description for most head-on type collisions. If the energy loss is very small, the excitation is an ordinary "exciton." The situation for energy losses around 15 to 25 eV is much less clear. Here the resonance coupling of adjacent

excited molecules is expected to be very large, so that the best description is probably significantly different from ionization. The density of excited states at such excitation energies is high. It is also clear that at energies above 20 eV or so the density of excited states is higher for those excited states that involve the excitation of more than one electron than for states that only involve one electron. Therefore, it would appear likely that initially formed excited states in this energy region would cascade through a sequence of states (in radiationless transitions) until the remaining excited states involved a maximum number of excited electrons.

The radical diffusion model for the radiation chemistry of water, discussed below, requires that H and OH radicals be formed in distributions that are quite confined, i.e., having a total breadth of 20 to 30 Å at most. Such a distribution is actually not inconsistent with an initial excitation described by a considerably larger wave packet. The several radical pairs formed in one spur arise from reaction or dissociation of excited molecules that remain after the cascade of radiationless transitions has been completed. Such excited molecules must have positions that are correlated, and, in fact, quite close together because the interactions producing the transitions are relatively short-range electron-electron interactions.

The radical diffusion model of the radiation chemistry of water provides a means for obtaining information on spur structure in water. No comparable effort has gone into the establishment of a tentative radical diffusion model for any other system. It is true, however, that radiation chemists have been generally aware of track effects and diffusion-controlled processes and have used them frequently in mechanisms. In fact, there has been an increasing attention to diffusion-controlled processes in the general field of mechanisms, both in photochemistry (32) and organic mechanisms (33, 34).

The spur model for the effect of γ -radiation has been very useful in the design and interpretation of experiments. Hamill (35) has discussed experimental work involving mixtures of hydrocarbons and various second components such as alkyl halides. Effects of second components on the yields of products normally observed in radiolysis of the principal component typically differ in three concentration regions. (a) At very low concentrations, below 10^{-3} in mole fraction, scavenging effects are readily observable. Intermediates that escape from spurs can react with a second component in such low concentration. Effects attributable to electronic excitation transfer to the solute are also observed. (b) At a concentration around 0.01 to 0.05 mole fraction another type of interference with the normal substrate reaction occurs. It is in this range that reactions normally attributable to electron attachment are observed. Sometimes such results have been literally interpreted in terms of the most naive model of a spur as one or more ionized molecules with their electrons escaping in random-walk path (36). One can only conclude that the electrons are recaptured before they collide with very many molecules, thirty or forty at most. (c) At concentrations of the second component above about 0.1 mole fraction a "direct" effect is usually observed. It is well to re-

member that in this region all electronic states of the mixture involve excitation of both kinds of molecules and that "direct" cannot refer to original excitation.

It is beyond the scope of this article to discuss details of this evidence [see (35)]. However, we can summarize that electrons do not appear to escape from spurs in chemically significant numbers in the systems so far studied. Spurs would seem to contain 20 to 30 molecules in systems of moderately small molecules such as cyclohexane, benzene, etc. This conclusion is in general agreement with the size of spurs as obtained in the radical diffusion studies of aqueous systems.

Electrical conductivity provides a very sensitive measure of free charge concentration. The track model discussed above predicts a certain amount of charge separation even if parent spur recapture is essentially complete. Approximately half of the energy is lost in delta rays and each delta ray has a net positive charge at its point of origin and an extra electron in the last spur it produces. According to Equation 7 we expect the number of delta rays per unit track length

$$NZ \int_{\epsilon_0}^{2mv^2} \frac{d\epsilon}{\epsilon^2}$$

where ϵ_0 is the minimum energy assigned to such an event. This consideration leads to an estimated G value for charge separation of

$$\approx \frac{100}{\epsilon_0} \left(\ln \frac{2mv^2}{I} \right)^{-1}$$

for a heavy charged particle, where ϵ_0 is to be taken in ev. For fast particles of interest here, the predicted value is $G \approx 0.1$.

Recent studies have been made of the conductivity of irradiated organic materials, chiefly plastics (40, 41, 42). Interpretation of this work depends upon a model containing several parameters as yet uncertain, but the results seem to be in general agreement with our discussion of track structure. It can be summarized that a plastic under irradiation obtains a conductivity σ , given by the relation

$$\sigma \propto R^\Delta \quad 11.$$

where R is the rate of irradiation and Δ is a number between 0.5 and 1.0. For a great many materials the following relation holds:

$$\sigma \approx 10^{-18} R \quad 12.$$

where σ is expressed in (ohm cm.)⁻¹ and R is in rads/minute.

In the conductivity model (40) only free electrons conduct current. Most of the separated charges are positive ions and trapped electrons with zero mobility. In terms of the mobility μ of a carrier with charge e in concentration n the conductivity is

$$\sigma = en\mu \quad 13.$$

In an irradiated system the number of free electrons present equals the num-

ber formed per unit time, multiplied by their mean life τ in seconds and we have

$$n = 10^{12} \frac{R\tau}{W} \quad 14.$$

where W is the number of electron volts required to furnish a free electron to the conduction band. Substitution of 13 and 14 into 12 (with e in coulombs) gives the relation

$$W = 1.6 \times 10^{11} \tau \mu \quad 15.$$

Fowler (40) found that $\tau \approx 10^{-7}$ to 10^{-8} for many substances. The value $\mu \approx 1$ has been used by Fowler (45) and observed by LeBlanc (43, 44), and we get the estimate

$$W = 1.6 \times 10^3 \text{ to } 1.6 \times 10^4 \quad 16.$$

The G values indicated by the range of Equation 16 is 0.6 to 0.006.

One other aspect of spurs is the low-grade heating that results from the energy degradation. One of the earliest explanations of the chemical action of high-energy radiations was the "point-heat" theory of Dessauer (37). The question of the effect of heat on radiation chemistry is discussed from time to time, but it is generally believed that no significant contribution from such effect exists in the action of low LET (linear energy transfer) radiations. Of course some of the energy remains stored as electronic excitation and potential energy of dissociation for a considerable time, but most is reduced to low grade heat during the time of a few molecular vibrations. Estimates of the initial temperature increase of an isolated spur range from 50° to 100°. It is not known that the macroscopic heat flow equations apply, but if they are approximately obeyed, the temperature T at a distance r from the center of the spur falls with the time as

$$T = T_0 + \frac{\Delta T \exp \left[-\frac{r^2}{r_0^2 + 4Dt} \right]}{\left(1 + \frac{4Dt}{r_0^2} \right)^{3/2}} \quad 17.$$

where we have assumed that the initial excess temperature has a Gaussian shape with the distribution parameter r_0 , and $D = \kappa/C_v$ is the (macroscopic) heat conductivity divided by the (macroscopic) specific heat. With $D \approx 10^{-3}$, which should apply to most liquids of present interest, a spherical spur cools too fast for reactions with activation energy to occur. In approximately 10^{-9} sec. the excess temperature is not more than the order of a degree anywhere. On the other hand, this situation is different for high LET radiation such as fission fragments and perhaps even for α -particles. For such cases there are no isolated spurs, but continuous columns of excitation. The initial temperatures are higher and the cooling rates are slower because there is cylindrical, not spherical, symmetry. For such cases there can be true thermal effects, as pointed out by Goldansky & Kagan (38) and Galanin (39). We shall not be concerned with this effect.

ELECTRONIC EXCITATION IN CONDENSED SYSTEMS

In this section we shall consider three types of investigations that bear on the behavior of electronic excitation in condensed systems: the loss spectra of electrons in thin films, the electronic spectra of polyatomic molecules, and the light yields of scintillator solutions. Experimental and theoretical aspects of each have been considered in the recent literature. Until recently the first area was of concern to physicists only; the other two areas have been studied by radiation chemists for some time.

Ruthemann (46) observed that, on passing through thin metallic films, electrons of energy in the vicinity of 30 kev suffered losses that were integral multiples of certain characteristic values. Pines & Bohm (47, 48) developed a theory of the phenomenon based upon excitation of plasma frequencies of the conduction electrons. It was later found that films composed of molecular materials such as metallic oxides and organic compounds exhibit the same effect, and the situation was somewhat more complicated than first believed [Marton *et al.* (49)]. Research activity in this field has continued at high level (69 to 73). A recent review has been given (10).

The energies of excited electronic states of condensed molecular materials are expected on theoretical grounds to differ from the energies of the excited states of the isolated constituent molecules (50, 51). The loss spectrum for a chemical compound, therefore, must depend upon its state of aggregation; for example, one would not expect to find the loss spectra of Figure 1 for *liquid* O₂ and N₂. On the other hand, it is well-known that the stopping power does not depend very strongly upon state of aggregation. Therefore, the overall rearrangement of oscillator strength cannot be very great.

The properties of the lowest excited electronic states must determine the ability of excitation energy to migrate in any system. From exciton theory it is known that both the energy level structure and the migration rates are determined by the interaction of neighboring molecules. Therefore, the absorption spectra of small polyatomic molecules gives precise information about the transfer of excitation energy [Kasha & McRae (52, 53)]. Although this phenomenon is understood quite well in a general way, very little attempt has been made to make specific applications to chemical effects. In an early paper, Franck & Teller (74) discussed the general situation and speculated about energy transfer in photosynthesis. Davydov (54) considered exciton theory for the special case of molecular crystals. The theory for non-crystalline materials such as liquids has not been worked out, but it is generally believed that the effects are similar.

In radiation chemistry the most typical primary energy absorption will involve the formation of two or more excitons in correlated positions. The occurrence of chemical effect usually requires the dissociation of a molecule, and if such a molecule is strongly coupled to its neighbors, the dissociation process may be affected. The author has considered some of these problems (31, 75). Exciton theory is involved, but certain modifications are necessary and the application has not yet been made in a satisfactory way.

The study of luminescence in liquid systems has yielded important information on the transfer of electronic excitation. Organic liquids such as benzene, toluene, cyclohexane, or a mixture of such liquids with a luminescent solute such as terphenyl, produced luminescence when irradiated with high-energy radiations or ultraviolet light (55). It is an interesting experimental fact that the characteristics of such systems are generally the same for irradiation by high-energy radiations and by ultraviolet light (56). This fact demonstrates that the significant excited electronic states that can transfer energy have excitation energies low enough to be excited by ultraviolet light. It should be noted, however, that only a relatively small amount of the absorbed energy is involved in luminescence. Estimates of maximum yields are in the vicinity of one or two per cent of the absorbed energy.

The mechanism of transfer of electronic excitation in solutions has been considered extensively (56 to 61; 63, 77). It is generally believed that the most important transfer mechanisms involve radiationless transfer, either by means of direct transfer over distances up to 50 Å [as emphasized by Förster (58, 59)], or by means of a migration of the energy through the solution to the recipient. Birks (60, 61) and Basile & Weinreb (76) have presented evidence that a radiative mechanism may be important at low solute concentration. In the case of scintillator solutions with benzene and cyclohexane as solvents, the transfer of energy from solvent to scintillators and to quenchers is fast enough to be puzzling. Lipsky & Burton (56) have suggested that a local ordering of the solvent molecules into domains, involving perhaps 10 or 15 molecules that are essentially excited as a unit, could explain the magnitude of the transfer and quenching constants [see also (62)]. Such a domain structure is in agreement with x-ray studies (64). On the other hand, it is difficult to understand why domains would be strongly coupled in the particular electron states presumably involved (65).

A powerful tool in the study of energy transfer in scintillator systems is the measurement of decay times of luminescence. Such measurements have been made by Swank *et al.* (66) and Burton *et al.* (67, 68). The latter authors have improved their technique so that the assumption of simple exponential decay is not made. Decay curves are usually found to be composed of two or more distinct parts, and lifetimes can be assigned separately to the scintillator and solvent.

Transfer of electronic energy has long been used as an elementary process in proposed mechanisms of radiation action. In the recent literature, Cramer & Burton (78) find that they must postulate a transfer of electronic energy from solvent to solute to explain the decomposition of organo-metallic compounds in benzene solution. Krongauz & Bagdasar'yam (79) propose a similar mechanism for the decomposition of benzoyl peroxide in aromatic solvents. *G* values attributed to this effect are usually well below unity. However, MacLachlan (80) used an energy transfer mechanism to explain a *G* value of 4 for the decomposition of certain benzyl compounds in cyclohexane. The magnitude of this yield would appear incompatible with other results,

and the possibility that a free radical mechanism is involved should be explored further.

RADIATION CHEMISTRY OF AQUEOUS SOLUTIONS

Aqueous solutions have been investigated more than any other systems in radiation chemistry, a situation partly the result of biological interest. Lea (81) discusses early work in the field and gives much information on ranges of charged particles and the track structure estimated for water. At the present time, work in this area is more sophisticated than that in any other area of radiation chemistry. All investigators use models extensively and frequently their objectives in studies are to check fine points in such models. The fact that different models still exist demonstrates that the subject is far from closed. For example, in spite of the relatively sophisticated nature of the work it is not known what intermediate species occur. Although it is generally agreed that the radicals H and OH are very important, there is no agreement about the roles (if any at all) of H_2^+ , H^- , the solvated electron, etc. This matter is considered further later. Recent reviews have been given by Hochanadel (82) and Allen & Schwarz (83).

The radical diffusion models.—Work in diffusion kinetics has been reviewed by Kuppermann (84). All radical diffusion models have in common a consideration of the diffusion-controlled reaction of radicals in tracks. They also usually consider H and OH as the principal radicals. The set of equations

$$\frac{\partial C_j}{\partial t} = D\nabla^2 C_j - \sum_i k_{ji} C_i C_j - \sum_s k_{sj} C_s C_j + \sum_i \tilde{k}_{ji} C_i + \sum_{m,n} \tilde{k}_{jmn} C_m C_n \quad j = 1, 2, \dots$$

is approximately solved with various initial conditions. Here C_j , C_i , ... are concentrations of the various radicals, C_s is the concentration of a scavenger, and the k 's are appropriate reaction rate constants for disappearance and appearance of the j th radical. Most studies have actually used a one-radical approximation. Samuel & Magee (23) introduced such a model which emphasized the initial geometrical distribution of radicals. It was stated explicitly that the H and OH radicals were distributed in spherical spurs with approximately the same distribution parameter in the case of low LET radiations. The track was visualized as a string of beads (i.e., spurs), and the principal effect of variation in LET was taken to be the alteration in the average distance between spurs. Ganguly & Magee (85) considered effects of LET and the random distribution of spurs for the one radical approximation. This theory has been quite successful in describing the LET dependence of aqueous systems (86, 92). Flanders & Fricke (87) and Fricke & Phillips (88) have investigated, with the aid of a digital computer, the one-radical model. A more elaborate investigation of this model using a two-radical approximation has been made recently by Dyne & Kennedy (89, 90). Still more elaborate studies, using different initial distributions of two radicals primarily formed, and following the simultaneous diffusion and reaction in a realistic sequence, have been made by Kuppermann (84, 91).

Studies of diffusion models have led to a good understanding of the diffusion-reaction competition and show that in a general way the theory adequately explains experimental results. As the theory becomes more elaborate, more parameters appear and at present they must be treated in an *ad hoc* manner. It is unlikely that further progress can be made until other points regarding species that occur, their reaction sequences, etc. are settled. The "string of beads" model ignores specific effects of delta rays. It is unlikely that all fine points of experimental results can be explained without explicit treatment of delta rays.

Gray (25) and Burch (24) give treatments that are radical diffusion models in spirit but are difficult to compare with the models discussed above. Gray's treatment generally ignores geometrical considerations, whereas Burch used a column model of the track in all cases. Collinson, Dainton & Kroh (115) report that Burch's prediction of the variation of yield with LET for alpha-particles is in agreement with experiment.

The establishment of the concept of the "molecular" and "radical" yields by Allen *et al.* (95) in the radiolysis of water, together with the radical diffusion model, led to an understanding of the effects of scavengers. The "molecular" products H_2 and H_2O_2 are formed by reaction of H and OH radicals in spurs according to the model. To first approximation, molecular and radical yields are constant for low scavenger concentration. Table I sum-

TABLE I
EFFECTS OF pH, D_2O , AND TEMPERATURE ON DECOMPOSITION
OF WATER BY GAMMA RAYS

	Neutral		0.4 M H_2SO_4		
	H_2O , 25°C.*	D_2O , 25°C.**	H_2O , 25°C.†	H_2O , 65°C.§	D_2O , 25°C.††
GH_2	0.45	~0.28	0.45	0.43††	0.38
GH_2O_2	0.71†	—	0.79	0.75	0.79
G_H	2.75	~3.24	3.63	3.79	3.94
G_{OH}	2.23	—	2.95	3.16	3.12
$G(-H_2O)_{net}$	3.65	~3.80	4.53	4.66	4.70
$G(-H_2O)_{gross}$	5.0	—	6.0	6.1	6.1
% radicals combined	50	—	46	43	42

* [Hochanadel (96)].

† [See Allen & Schwarz (83)].

** [Hardwick (97)].

‡ [See e.g., Sworski—values corrected to zero scavenger concentration (99)].

§ [Ghormley & Hochanadel, unpublished].

†† [Mahlman & Boyle—values corrected to zero scavenger concentration (98)].

marizes experimental results as presented by Hochanadel (82). Coatsworth, Collinson & Dainton (116) have reported recent experimental work covering much of the range of Table I and agree very well, although some of their values differ more than their estimated errors.

Mechanism studies.—Much of the recent work on solutions has been concerned with establishing the mechanisms of action of radiations. The most complete discussion of the mechanism of the radiolysis of water, including rate expressions for solutions containing various amounts of H_2 and H_2O_2 , has been given by Allen & Schwarz (83). Ershler, Nezhevenko & Miasishcheva (93) have made a complete analysis of the special case of solutions of H_2O_2 . The radiolysis of formic acid solution has been considered extensively by Smithies & Hart (94).

Rotblat & Sutton (100) have investigated the effects of high dose rates on the radiolysis of ferrous sulfate and ceric sulfate. Dose rates ranged up to 10^{10} rad/sec. in pulses of 10^4 rads. The results at the highest dose rates were explained in a satisfactory quantitative manner by considering the accepted sequence of radical reactions in the homogeneous distribution resulting from the merging of neighboring spurs. Under such conditions no diffusion-controlled processes are of importance. A previous high dose rate study of the reduction of methylene blue in dilute solution was reported by Hutchinson (101).

Intermediates in irradiated water.—Many proposed mechanisms in the radiolysis of aqueous solutions employ the radicals H and OH as the only intermediates of chemical importance formed from water. It is clear that the situation is actually much more complicated, and much speculation exists about other entities that may occur and about their possible roles. At various times almost all intermediates of the possible types $(H_nO_m)^{\pm q}$ have been proposed (for n, m, q , zero or positive integers). The most definite advance made recently is the proof by Barr & Allen (102) that two kinds of reducing entities are formed; these are frequently said to be two kinds of "H atoms" and, in fact, are usually called "H" and "H'." One of these atoms is presumed to be the ordinary H atom and the other was suggested by Barr and Allen to be either H_2^+ or the solvated electron.

The use of H_2^+ is generally attributed to Weiss (103). This entity has often been used in mechanisms of radiolysis, e.g., the oxidation of ferrous sulfate (104). Czapski *et al.* (105) have recently used H_2^+ in explaining the oxidation of iodide ion in solution by means of H atoms introduced into the solution from a high frequency gaseous discharge. Kurien & Burton (106) have studied the radiolysis of H_2O_2 in D_2O and report that no chemically significant entity HD^+ is present. The work of Kurien and Burton is so clear-cut that no misinterpretation seems possible. It appears to the author, therefore, that the previously assigned role of H_2^+ may be incorrect.

One of the most controversial intermediates in water is the electron. Scavenger studies seem to indicate that very few if any electrons are released from their parent spurs. Recently, Hart (107) suggested that subexcitation

electrons (108) could be responsible for a G value of the order of unity at a solute concentration (formic acid) of 0.1 molar. It is hardly questioned that subexcitation electrons can be important, although it is well to remember that the lowlying electronic states of systems such as liquid water are complex (see earlier section) and an effect now attributed to subexcitation electrons may later require re-interpretation in terms of electronic excitation transfer. The question of the "solvated electron" is even more complicated. Barr & Allen (102) say that their "H" atom may, in fact, be a solvated electron.

The elementary processes in the action of radiation on water have been re-examined by Fiquet-Fayard (109) along the lines of Laidler (110) except that a more explicit application to the liquid state is attempted. The question of the formation of H_3O^+ from the reaction of H_2O^+ with a neighboring water molecule in irradiated water was considered by Fiquet-Fayard (111) who estimated, on the basis of ion-molecule reaction rate constants observed in the gas phase, that such a reaction should occur in 10^{-12} to 10^{-13} sec. The H_3O^+ entity has been mentioned previously (112) in connection with the more general question of the effects of hydrogen bonding on the elementary reactions of liquid water in radiolysis. It is well-known from spectroscopy that the intermolecular potential function of the OH bond is considerably altered by hydrogen bonding (113), and it seems likely that the ion-molecule reaction time is considerably less than the above estimate and may be as small as 10^{-14} sec. In any case, the products $\text{H}_3\text{O}^+ + \text{OH}$ should be formed in good yield, since parent-ion electron recapture cannot prevent occurrence of the ion-molecule reaction.

Platzman (114) has revived interest in the entity H^- . He suggests that the capture of an electron in neutral water to yield $\text{H}^- + \text{OH}$ would be followed by $\text{H}^- + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}^-$. It has often been said that part of the "molecular" products do not originate from recombination of radicals. On the other hand, it is unlikely that this particular process accounts for a substantial fraction of the H_2 yield. In short, the success of the radical diffusion model militates against such a possibility.

STUDIES OF MECHANISM IN NON-AQUEOUS SYSTEMS

The action of high-energy radiations on non-aqueous systems is generally believed similar to their action on aqueous solutions, but we have no example of a well developed model comparable to the radical diffusion model for the latter case. Some of the current work in this area is still largely exploratory in nature. The most-studied system is the " C_6 system": cyclohexane and benzene, and their mixtures and solutions. This system was first studied because cyclohexane is a typical aliphatic compound with a fairly high sensitivity to radiation whereas benzene was said to be very resistant. Furthermore, cyclohexane has only one kind of hydrogen atom. It is evident that many effects can be investigated in such systems: protection, sensitization, energy transfer, etc.

In most systems, as in aqueous systems, a mechanism involving only a sequence of radical reactions provides a framework for understanding the action of radiation. In fact, many authors actually look upon the action of high-energy radiation merely as a source of radicals [cf. Lucchesi & Bartok (117)]. Closer examination usually shows that a radical mechanism is inadequate in essential details and that other intermediates must be involved. However, because of the great importance of radicals in radiation chemistry the use of EPR (electron paramagnetic resonance) has become an important tool in mechanism studies. This technique has not been as successful as first expected, primarily because of the short lives of the radicals under the conditions of most interest. Charlesby (3) and Swallow (4) have reviewed the early literature. A recent study is reported by McConnell *et al.* (118).

The C₆ systems.—A mechanism that explains all the observed phenomena of the C₆ systems does not yet exist. We shall consider some aspects of these systems, emphasizing the recent literature. Authors have used diffusion-controlled reactions of radicals, hot reactions, energy transfer, ionic reactions, and ultimate molecule formation in their various proposed mechanisms. The general features of the radiolysis of *n*-hexane and cyclohexane can be understood on the basis of the primary breaking of a C—H bond with a $G \approx 5$ followed by a relatively simple sequence of reactions (cf. Dewhurst, 119, 120). For cyclohexane, e.g., the principal products are hydrogen gas, cyclohexene, and dicyclohexyl. Dewhurst & Schuler (121) and Schuler (122) have investigated the effect of LET and report that the diffusion-controlled track reactions are less important than in aqueous systems. Schuler & Muccini (123, 124) and Dyne & Fletcher (126) have investigated the effect of dose rate. All of these results appear interpretable on the basis of a radical diffusion model.

Dewhurst (120) and Dyne & Jenkinson (125) have presented evidence that some of the H₂ gas in cyclohexane radiolysis is formed directly by the decomposition of an excited molecule. The original evidence of Dewhurst was on the basis of scavenger action, and it was concluded that the direct decomposition had a $G(\text{H}_2)$ value of 0.7. Dyne and Jenkinson investigated mixtures of C₆H₁₂ and C₆D₁₂ and found that the unimolecular D₂ production from C₆D₁₂ has $G(\text{D}_2) = 0.25$, which they conclude is in general agreement with Dewhurst's measurement of $G(\text{H}_2)$ in C₆H₁₂ since the latter is expected to be larger because of the isotope effect. The formation of H₂ by unimolecular decomposition is a recognized process in gas phase investigations; Dorfman (127) first reported the effect in ethane radiolysis.

In an extensive investigation of the radiolysis of mixtures of cyclohexane with many second components and scavengers, Forrestal & Hamill (128) concluded that the H₂ yield can be separated into three parts: one due to thermal H atom attack on cyclohexane with $G(\text{H}_2) \approx 2.0$; one due to processes with ionic precursors, with $G(\text{H}_2) \approx 3.0$; and the third due to "hot" H atom attack on cyclohexane with $G(\text{H}_2) \approx 0.85$. Nevitt & Remsberg (129) also have concluded through scavenger studies that the yield of H₂ resulting from thermal radical reactions cannot be more than 40 per cent, and the yield due to direct detachment cannot be more than 25 per cent of the total,

but they do not speculate on the origin of the remainder. Hardwick (130) has proposed a radical mechanism involving hot H atoms; he has suggested that the molecular product could be due to a radical reaction involving caging. However, it seems unlikely that the results involving formation of D_2 could be explained on this basis.

Forrestal and Hamill consider charge transfer, electron attachment, and energy transfer; all of these processes have possible roles in the mechanism. In that paper (128) and previously, Hamill (35) points out that molecules known to have high dissociative attachment cross sections in the gas phase, such as CH_3I in the process $CH_3I + e^- \rightarrow CH_3 + I^-$, do not appear to attach electrons very efficiently in liquid mixtures. If free electrons were released into a mixture of cyclohexane and CH_3I , at very low concentration of the CH_3I , changes in the product distribution could be observed if the dissociative attachment occurred. In fact, CH_3I must be in ~ 5 per cent fraction before such changes are observed. Even on the simple electron recapture picture of the spur, one would expect a relatively greater effectiveness of such an additive. The model of a liquid as a highly compressed gas is obviously inadequate. The electronic states and dissociation processes are influenced by the state of aggregation and a more satisfactory description must be found.

Freeman (131, 132, 133) has investigated cyclohexane and its mixtures with benzene and with cyclohexene. He has interpreted the chemistry in a mechanism involving excited molecules, radicals, hot H atoms, and excitation transfer. Scavenger studies that clarify the roles of halogen scavengers have been reported by Meshitsuka & Burton (134) and Hughes & Garrison (135).

Ions and excited states as intermediates in the gas phase.—Futrell (136, 137) has presented a simplified mechanism to explain the radiolysis of gaseous *n*-hexane and *n*-pentane. Reaction is supposed to be initiated only by ionization; the distribution of ions is taken as that of the low pressure mass spectrometer patterns; each ion is supposed to react with a neutral molecule in a hydride ion transfer reaction as proposed by Field & Lampe (138); a simple radical sequence follows. Futrell has done the bookkeeping on this model and finds remarkable agreement with experimental observations in both cases.

In contrast with this result, Mains & Newton (139, 140) have studied the photolysis of methane and compared it with the radiolysis of methane in the presence and absence of mercury vapor. They compare the reactions for cases in which ions are formed with cases in which ions cannot be formed. The results are in striking agreement for all cases, both in products and in product distribution. Williams (141) has shown that irradiation of methane with electrons of energy below the ionization potential gives the same results. It is clear that, in those cases in which ions are formed, they do have a role since the reaction $CH_4^+ + CH_4 \rightarrow CH_3 + CH_5^+$ has been shown to occur by Martin & Melton (142).

It is easy to demonstrate that irradiation of a gas produces at least as

many excited electronic states as ions. Since it is known from photolysis studies that excited electronic states react, and, in fact, produce the same products as radiolysis in the case of CH_4 , it is reasonable to assume that they are effective intermediates in radiolysis. The results of Futrell (136, 137) are perhaps surprising only because the yield of products is lower than one might expect on the basis of reaction of both ions and excited molecules.

Lampe (143) has produced evidence that ion molecule reactions occur in gas phase radiolysis by showing that the radiation-induced hydrogenation of ethylene is sensitized by the addition of gases X, which are known to undergo the reaction $\text{X}^+ + \text{H}_2 \rightarrow \text{XH}^+ + \text{H}$.

Melton & Rudolph (144) have developed a high-pressure alpha-particle mass spectrometer that allows a direct observation of ionic intermediates. The ions they observe come from an ionization chamber at a pressure as great as 1 mm. and hence many collisions occur before the ions reach the acceleration tube. They have studied charge transfer in hydrocarbon systems (145), the radiolysis of ethylene (146), mechanism of charge transfer reactions (147), and the intermediates in the polymerization of cyanogen (148). This instrument promises to be a very valuable addition to the techniques available to radiation chemistry. The ionic intermediate $[\text{Xe}(\text{CN})_2]^+$ was found in the radiolytic polymerization of CN as Eyring (149) had postulated. Although it is verified that Xe^+ has chemical reactivity, Rudolph & Lind (150) found it to have no effect on the radiolysis of CO.

Henglein & Muccini (151) have studied ion molecule reactions in various systems containing I_2 . Various ions such as CH_4I^+ were found. This particular ion appeared to come from the reaction of an excited I_2^+ ion, $\text{I}_2^{+*} + \text{CH}_4 \rightarrow \text{CH}_4\text{I}^+ + \text{I}$. Other ion-molecule reactions of excited ions have been reported by Cermak & Herman (152).

Ionic condensation and polymerization.—The radiation chemistry of polymers and polymerization has been treated almost entirely as radical chemistry. It has been reviewed recently by Charlesby (3, 153). Cationic polymerization, known for a long time [Plesch (154)], has recently attracted the attention of radiation chemists because it can be initiated by high-energy radiations and seems to be a tool for probing of the elementary processes of the action of radiation. Collinson, Dainton & Gillis (155) and Magat (156) have considered the mechanism of ionic polymerization from this point of view.

Many radiation-induced ionic polymerizations are known, but the polymerization of isobutene appears to be the most-studied example. If chemical initiators are used, it is generally assumed that charge separation leads to the formation of a carbonium cation that carries the chain; the location of the anion relative to the cation is not explicitly considered, but apparently no one thinks the charges are widely separated. The G value for the radiation initiation of ionic polymerization in pure isobutene is 0.19, and compares favorably with the estimate made above of $G \approx 0.1$ for charge separation in delta rays. Supporting the point of view that ionic polymerization requires

charge separation is the fact that additives, such as metallic oxides that could conceivably trap electrons to prevent spur recapture and promote the initiation yield, increase it to a maximum G of 2 or so.

A radiation-induced reaction that is perhaps a clearer example of an ionic mechanism has been reported by Wagner *et al.* (157, 158). The radiolysis of liquid propylene at -40° and -78° yields mainly dimeric and trimeric products that cannot be explained on the basis of free radical processes and must be attributed to an ion-molecule condensation. Some products formed in smaller amounts apparently result from radical processes. The dimerization of the terminal olefins hexene and octene (158) were also studied. The mechanism proposed by these authors is easy to understand on the basis of accepted concepts of radiation chemistry. It should be mentioned again that in condensed phases ion-molecule reactions involving hydrogen atom transfer are expected to compete favorably with parent spur recapture of electrons.

SUMMARY AND CONCLUSIONS

A theoretical framework exists for the understanding of chemical effects of high energy radiations. In a general way a great many systems are understood, but closer examination always reveals that much remains to be explained. It appears to the author that the greatest need is for a better understanding of elementary processes. The elementary processes of the gas phase can be studied theoretically and experimentally with available techniques, and for this reason radiation chemistry of the gas phase may be the most profitable area for investigation. However, examination of the current literature indicates that very little gas phase work is in progress. The radiation chemistry of condensed phases seems to hold more of a challenge. In many ways such systems are deceptively simple. It usually appears that a sequence of radical reactions is adequate to explain the observed results, but on closer examination it is evident that non-radical processes must also occur. Furthermore, the initial identity and geometrical distribution of the radicals are unknown. The theory of radiation effects in condensed systems has not been developed to the point of being a very great help. Experimentalists and theorists both tend to think of liquids as condensed gases rather than as distinct systems with characteristic properties of their own. Theoretical progress is likely to be slow and the radiation chemistry of liquids may continue for some time to appear both simpler and more complicated than that of gases.

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KINETICS OF GAS PHASE REACTIONS¹

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The papers published during the past year reflect the enhanced interest in both the theoretical and the experimental methods of investigating (a) the basic assumptions of the existing theories of unimolecular reactions and (b) reactions involving atoms. There has been progress in the accumulation of information about the rate constants of elementary radical reactions through the study of additional reaction systems, the use of new and improved experimental techniques, and the application of computer methods to the treatment of rate data. To keep the present review within the prescribed limits, references to the contributions of earlier workers have had to be omitted and many articles, particularly those in the field of oxidation, could not be included. Within the year the comprehensive book on kinetics by Benson (1) and one concerning isotope effects (2) have appeared. Most of the papers from a symposium about atomic reactions held at McGill University, Montreal, on September 6-7, 1960 have been published in the October 1960 issue of the *Canadian Journal of Chemistry* and many of these will be referred to individually in the material that follows. Reviews have been written about Arrhenius factors in unimolecular reactions (3), shock waves (4), and primary processes in photo-oxidations (5).

THEORETICAL DEVELOPMENTS AND TESTS OF THEORIES

A number of significant publications have dealt with two important problems of unimolecular reaction rate theory. The first problem concerns the question of whether activation-deactivation in unimolecular reactions occurs by stepwise processes or by strong collisions. The second involves the question of whether unimolecular reactions behave more in accord with (a) the Slater assumption (6) of no redistribution of internal energy among the normal modes between collisions or (b) the Rice-Ramsperger-Kassel proposal (7) of energy passing from one to another of the oscillators. Buff & Wilson (8) have critically analyzed both aspects and have presented a general theory for these effects. For trace amounts of reactive molecules the observed rate constant may be identified with the lowest eigenvalue of the resulting relaxation spectrum. They also calculated the pressure dependence to be expected for unimolecular reactions on the basis of the Kassel molecular decomposition frequency and of stepwise activation among neighboring vibrational states having Landau-Teller transition probabilities (9). To account for the pressure dependence of the rate constant between the high and low pressure limits, the inefficient collision mechanism requires a model

¹ This review has been prepared from the literature available by November 17, 1960, but the Russian literature was from the previous year.

with about two fewer Kassel oscillators than that needed for the strong collision mechanism. Buff & Wilson concluded that the inefficient collisional process and anharmonic effects in the intramolecular process tend to broaden the transition range. The Buff-Wilson treatment for the case $s=1$ was found to agree with the work of Montroll & Shuler (10) on the low pressure limit of diatomic molecules.

The importance of the problem of the collision efficiency for deactivation of highly excited molecules has been emphasized in an earlier review [Johnston (11)]. Mahan (12) has advocated the hypothesis of collisional processes involving small changes in the vibrational energy of such molecules and has cited evidence from the existing data. Of interest in this connection are the recent findings of Rabinovitch and his co-workers who studied the unimolecular decompositions of vibrationally excited radicals produced by the addition of an H or D atom to an unsaturated hydrocarbon (13, 14, 15). For *sec.*-butyl- d_1 radicals, the ratio of decomposition D to collisional stabilization S has been measured for decreasing pressures at 25°C., and it was concluded that the collisional activation-deactivation assumption of strong collisions is supported by the data [Harrington, Rabinovitch & Hoare (15)]. Results for the change of D/S with pressure, in the case of ethyl- d_2 radicals, were also interpreted as corresponding to a collision efficiency of unity for the stabilization reaction (13).

The effect of weak intramolecular coupling upon the pressure dependence of the rate constant of a unimolecular reaction has been examined by Wilson (16). Experimental evidence relating to the question of the flow of energy between normal modes has been obtained by studying the reactions of the methylene radical. Butler & Kistiakowsky (17) have formed energy-rich methylcyclopropane molecules by (a) the reaction of methylene with cyclopropane and (b) the reaction of methylene with propylene. The composition of the mixture of butenes produced by the rearrangement of the methylcyclopropane was the same for both (a) and (b). They have concluded that the energy of the "hot" molecule migrates freely among the normal modes during the time between formation and reaction. The isomerization products from 1,1-dimethylcyclopropane have been compared for molecules excited thermally and for chemically activated molecules formed from methylene and isobutene [Frey (18)]. At first the results were interpreted as supporting the Slater model (18), but later this interpretation was withdrawn (19). Harrington, Rabinovitch & Frey (19) have found similar behaviors with respect to decomposition exhibited by *sec.*-butyl radicals formed in two different ways, namely, from H and D atoms with butene-1 and from H and D atoms with *cis*-butene-2, and the rate of the reaction depends upon the total excess energy. These findings were taken as an indication of the migration of internal energy among the vibrational modes before decomposition, as expected from the Rice-Ramsperger-Kassel model of coupled vibrations. In the thermal isomerization of methylcyclopropane, the decrease in k/k_∞ with pressure occurs at about 1/30 the pressure observed for a similar de-

crease in the cyclopropane rearrangement. Chesick (20) concluded that the magnitude of this shift in pressure dependence, as well as the similarity to cyclobutane, would not be expected on the basis of Slater's theory but could be explained by a model allowing for intramolecular energy transfer in the lifetime of the activated molecule.

A comparison of the shape of the fall-off curves predicted from the Slater and the Rice-Ramsperger-Kassel theories has shown that the relationship between the fall-off parameters n and s diverges from the expression $n = 2s - 1$ as s increases (21). Thiele & Wilson (22) have extended Slater's classical theory to a reaction where each of two internal coordinates must simultaneously exceed some critical value and Slater (23) has treated the same problem by the transition state method. The theory of the stochastic process has been applied by Ishida (24) to unimolecular and other chemical reactions. Rubin & Shuler (25) have shown that in the dissociation of a linear four-atomic molecule a greater probability exists for breaking an exterior bond than the interior one. The mass spectra of propane and propane-2,2- d_2 have been calculated on the basis of unimolecular decompositions of excited molecule ions (26). The results of the decompositions of excited alkylamine ions have been compared with those predicted by theories of unimolecular reactions (27). For the rate of dissociation of an electronically and vibrationally excited molecule, Porter & Connelly (28) have made calculations involving the use of unimolecular reaction rate theory.

The influence of the perturbation from the equilibrium Boltzmann distribution near the dissociation limit is considered by Nikitin & Sokolov (29) and Stupochenko & Osipov (30) in the calculation of the rate of dissociation of diatomic molecules. The decrease in the level population near the dissociation limit has been cited as the cause for the lack of agreement between certain observed rates of dissociation and the rate calculated from the recombination rate and the equilibrium constant. The expression for the second order rate constant for dissociation has been generalized to apply to polyatomic molecules, taking into account the quantization of the vibrations (29). The "ladder climbing" model of Montroll & Shuler (10) was used also by Shuler (31) for the calculation of the vibrational distribution functions of A_2 in the reaction, $M + A_2 \rightarrow M + A + A$. A general collision theory for reactions occurring as a result of binary collisions between reactant and inert gas has been proposed by Widom (32).

The reverse of the dissociation process for diatomic molecules has continued to receive theoretical consideration (33, 34, 35). Bunker (34) has discussed the mechanics of atomic recombination reactions and Keck (35) has proposed a variational theory for application to three-body recombinations. The rate of recombination of oxygen atoms, in the presence of an oxygen molecule as a third body, into oxygen molecules in vibrationally excited states has been calculated by a quantum mechanical perturbed stationary state method [Bauer & Salkoff (36)]. With respect to free radical combination reactions, Mahan (37) has concluded that the equilibrium assumption of

chemical kinetics is valid for photochemical experiments where the mole fraction of free radicals does not exceed 0.01, but it may not be valid for systems with mole fractions of radicals of 0.1 or greater.

For the calculation of the quantum mechanical probability of the exchange reaction $BC + A \rightarrow B + CA$, for constrained linear encounters, Mazur & Rubin (38) have developed a numerical procedure suitable for use with computers. Yamamoto (39) has proposed a theory of the reaction rate of gas-phase exchange reactions based on the quantum-statistical mechanical theory of linear irreversible processes. Rates of *ortho-para* and isotope exchange reactions of the type $H + H_2 \rightarrow H_2 + H$ have been calculated by the absolute reaction rate theory with new data for the shape of the H_2 surface and an empirically chosen activation energy [Shavitt (40)]. The formation of vibrationally excited species in reactions of atoms and molecules has been given special consideration in several papers. Polanyi (33) has shown that a valence bond resonance description of the activated complex in exothermic reactions, $A + BC \rightarrow AB + C$, will predict that the bond $A-B$ will contain almost all of the heat of the reaction. From a consideration of the molecular collision for this type of reaction, Smith (41) has suggested a method of calculating the fraction of the reaction energy that can appear in this vibration. For the reaction $A + BCD \rightarrow AB + CD$ similar results would apply to the bond $A-B$ and no excitation of the vibration in $C-D$ is predicted. In the collisional model proposed by Simons (42) much of the heat of the reaction will be found in $A-B$ if there is an attraction between A and B and a weakness in bond $B-C$. A comparison of the predictions of these theoretical models with the presently available data has been made by Basco & Norrish (43).

Herschbach, Johnston & Rapp (44) have obtained molecular partition functions in terms of local properties that are more convenient for use in chemical kinetics calculations. Wolfsberg (45) has discussed isotope effects on reaction rates and has compared the Slater approach (6) with the transition state theory approach (46). Further consideration of secondary kinetic isotope effects shows them to be small unless force constants involving isotopically substituted positions are much different in the transition state than in the reactant (47).

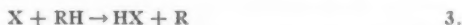
ATOMIC REACTIONS

Removal of a hydrogen atom.—McNesby, Scheer & Klein (48) have determined the isotope effect in the reactions of hydrogen atoms with formaldehyde. For the reactions



their measurements have shown $E_2 - E_1 = 1.0$ kcal./mole and $A_2/A_1 = 0.88 \pm .07$. The corresponding reactions with D in place of H have an activation energy difference of 0.9 kcal./mole. When the results were considered in terms of the Bigeleisen theory of the isotope effect (46), a loosely bound activated complex was indicated. From the photolysis of methyl mercaptan

the activation energy and the steric factor of the reaction, $\text{H} + \text{CH}_3\text{SH} \rightarrow \text{CH}_3\text{S} + \text{H}_2$, have been found to be about 4.6 kcal./mole and 0.34, respectively [Inaba & Darwent (49)]. The hydrogen transfer reactions of fluorine and bromine atoms with hydrocarbons have been studied by Fettes, Knox & Trotman-Dickenson (50, 51).



Some of the kinetic results for the fluorine atom reactions that they obtained by a competitive method are summarized in terms of A -factors and activation energies in Table I, which also includes rates for bromine atoms. For the

TABLE I
REACTIONS OF FLUORINE AND BROMINE ATOMS WITH HYDROCARBONS (51)

R-H	Fluorine Atoms		Bromine Atoms	
	$\log(A, \text{cc./mole-sec.})$	E kcal./mole	$\log(A, \text{cc./mole-sec.})$	E kcal./mole
CH_4	14.0	1.21	14.0	18.3
C_2H_6	13.7	0.28	13.9	13.4
$n\text{-C}_4\text{H}_{10} \text{ prim. H}$	13.3	0	—	—
$neo\text{-C}_4\text{H}_{10}$	13.7	0	14.2	14.3
$\text{C}_3\text{H}_8 \text{ sec. H}$	13.0	0	13.7	10.1
$n\text{-C}_4\text{H}_{10} \text{ sec. H}$	13.3	0	13.2	10.2
$iso\text{-C}_4\text{H}_{10} \text{ tert. H}$	12.8	0	13.3	7.5

fluorine series the value of the A -factor calculated for the reaction with ethane by the transition state method (52) was assumed to be correct and the activation energies for attack on hydrocarbons above ethane were taken as zero (50).

Combinations of atoms.—Engleman & Davidson (53) have measured the rates of recombination of iodine atoms in the presence of various third-body gases, such as H_2 , He, CH_3I , and C_6H_6 , at 323–548°K. Their findings are in general agreement with those of Porter & Smith (54). In the consideration of the data they have discussed the intermediate complex mechanism:



The suggestion (54) of a charge transfer complex between I and M was regarded as plausible for molecules such as benzene and methyl iodide, whose rate constants and negative temperature coefficients are large. The shock tube technique has been used for the determination of the rate of dissociation of molecular bromine in the presence of Ar, He, N_2 , CO, O_2 , and CO_2 at temperatures from 1300 to 1900°K. [Britton (55)]. Recombination rate constants were calculated from the relationship $k_R = k_D/K$ and the values at 1600°K.

were approximately an order of magnitude smaller than the rates from flash photolytic experiments near room temperature. Burns & Hornig (56) have devised a technique involving a combination of flash photolysis and the shock tube method for measurement of the recombination rate of bromine atoms at 950°K.

The recombination rates of nitrogen atoms have been determined at higher temperatures, up to 700°C. [Back, Dutton & Winkler (57)]. With the surface recombination of either first or zero order taken into account, the homogeneous rate constant increases with temperature. From spectroscopic examination of the emission from hydrogen-oxygen-nitrogen flames into which halogens had been introduced, Phillips & Sugden (58) proposed the overall processes 6 and 7. In their discussion they have considered direct



radiative recombination and stabilization by collision of an intermediate excited molecule.

Considerable attention has been given to evaluating the rate of recombination of oxygen atoms in the gas phase. The rate constant for the reaction



has been observed to be $k_8 = 9.8(\pm 1.1) \times 10^{14}$ cc.²/mole²-sec. in an oxygen-argon mixture at 300°K. [Reeves, Mannella & Hardeck (59)]. Under the experimental conditions (0.3 to 1.3 mm.) the consumption of oxygen atoms by the following reactions



was found to be about 10 to 20 per cent at the higher pressures. The reported value for k_8 was corrected for this effect. The authors have pointed out that in view of the value of 8.4×10^{14} cc.²/mole²-sec. obtained for k_8 at 3500°K. [Matthews (60)], very little temperature dependence of the rate constant is indicated. To avoid ozone formation Morgan, Elias & Schiff (61) prepared oxygen atoms by the reaction $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$ and measured the recombination rate of oxygen atoms essentially in the absence of O_2 . Their value for k_8 with N_2 as M was 3.2×10^{15} cc.²/mole²-sec. For k_8 with $\text{M} = \text{O}_2$, Kretschmer & Peterson (62) assigned an upper limit of 2×10^{14} cc.²/mole²-sec.

The rate of reaction 9 was investigated by Dickens, Gould, Linnett & Richmond (63) with oxygen atoms prepared by passing electrolytic gas with a small percentage of water vapor through a microwave discharge. The decay of the oxygen atom concentration was first order in oxygen atoms and second order in oxygen molecules in agreement with reaction 9 for $\text{M} = \text{O}_2$. The rate constant was 6.0×10^{14} cc.²/mole²-sec. at 283°K. For the same quantity and in the same units Kretschmer & Peterson (62) have observed k_9 to be 1.1×10^{14} at 350°K. From data of a different type, namely, the decomposition

of ozone, k_9 has been evaluated as 0.72×10^{14} cc.²/mole²-sec. for $M = O_2$ at 300°K. [Benson & Axworthy (64)]. With $M = O_3$, a more efficient third body, the rate expression of Zaslosky *et al.* (65) would give 1.54×10^{14} cc.²/mole²-sec. at 300°K. In the study by Kretschmer & Peterson (62) the oxygen atoms were prepared by electrodeless discharge and variable results were observed unless rigorous drying was used. They reported that the rate of decay in the presence of dissociated water vapor is several times larger than in dry oxygen. It is possible that the disturbing influence of dissociated water vapor has been present, but unnoticed, in other studies.

Other atomic reactions.—Investigations of much interest have been made on the reactions of oxygen atoms with organic molecules. Cvetanović (66) generated O (³P) atoms by the mercury photosensitized decomposition of nitrous oxide and measured the rates of addition to different olefins at 25° and 125°C. The results permitted ratios of pre-exponential factors and activation energies to be evaluated on a relative basis. The variation in the reactivity of the olefin with change in structure has been interpreted in terms of the electrophilic character of oxygen atoms (67). With 1,3-butadiene the oxygen atoms react by 1,2-addition to form butadiene monoxide and, presumably, 3-butenal [Cvetanović & Doyle (68)]. It was pointed out that the addition products possess excess energy as a result of the heat of the reaction and would decompose unless stabilized by collisional deactivation. In the reactions of oxygen atoms with olefins at very low pressures only products resulting from the fragmentation process would be observed. Elias & Schiff (69) have investigated the reactions of ethylene (and butane) with oxygen atoms from an electrodeless discharge. Their data gave the following rate constants: with ethylene, $k = 1.8 (\pm 0.6) \times 10^{-11} \exp(-1600/RT)$ cc./molecule-sec., and with *n*-butane, $k = 5.0 (\pm 1.6) \times 10^{-11} \exp(-4200/RT)$ cc./molecule-sec. The activation energy found for the ethylene reaction is somewhat lower than the 2.6 to 2.9 kcal./mole estimated by Cvetanović (66). Murad & Noyes (70) have studied the reactions of C_2H_6 with O (¹D) atoms from the photolysis of N_2O at 1900 to 2000 Å. One reaction produces ethylene and water in a single step and a second reaction with ethane yields other products. The oxygen atoms react with C_2H_4 about 330 times more rapidly than with C_2H_6 . The reaction $O + CO \rightarrow CO_2$, which was accompanied by a blue luminescence, was investigated at 421–555°K. [Avramenko & Kolesnikova (71)]. The second order rate constant was expressed as $k = 3 \times 10^{-15} T^{1/2} \exp(-3000/RT)$ cc./molecule-sec. A process involving ternary collisions was ruled out because the steric factor would then be too high. Rates of upper atmosphere reactions involving O and N atoms have been treated by a digital computer method (72). The diffusion flame technique (73) has been applied to the study of the reaction $O + NO + M \rightarrow NO_2 + M$.

As a result of observing the reactions of active nitrogen with NO and NO_2 , Verbeke & Winkler (74) concluded that more than one reactive species in active nitrogen reacts with NO and that a significant error may be involved in the measurement of the nitrogen atom concentration by the use of

the extent of the NO reaction. In the reaction of N atoms with C_2H_4 , Herron (75) assumed the formation of an intermediate complex (NC_2H_4) that could either react with another N atom yielding N_2 or decompose into products. Active nitrogen has been observed to destroy $(CN)_2$ with the formation of a black polymer [Haggart & Winkler (76)]. In this system CN radicals were formed and were able to react with hydrogen or methane to form HCN or CH_3CN , but the results did not support the view that the HCN formed in the reaction between active nitrogen and hydrocarbons results from the initial formation of CN radicals. For the first time, significant amounts of NH_3 have been found in the products of the reaction of active nitrogen with $C(CH_3)_4$ and other hydrocarbons [Dewhurst (77)]. In the reactions between active nitrogen and the methylsilanes the increase in the NH_3 /HCN ratio with in-

TABLE II
ATOMIC REACTIONS YIELDING VIBRATIONALLY EXCITED PRODUCTS

Reaction	Highest Vibr. Level of M*	Investigators
$H + HO_2 \rightarrow OH^* + OH$	3	Charters, Polanyi (80)
$O + NO_2 \rightarrow O_2^* + NO$	11(12?)	Basco, Norrish (43)
$O + O_3 \rightarrow O_2^* + O_2$	19(20?)	Basco, Norrish (43)
$O(^1D) + RH \rightarrow OH^* + R$	2	Basco, Norrish (43)
$S + S_2Cl_2 \rightarrow S_2^* + SCl_2$	12	McGrath (81)
$H + O_3 \rightarrow OH^* + O_2$	9	Garvin, Broida, Kostkowski (82)

† $RH = NH_3, H_2, HCl, CH_4$, and H_2O

creasing methyl substitution indicated that the hydrogens attached to carbon are involved in the formation of NH_3 [Dewhurst & Cooper (78)]. The reaction $K + HBr \rightarrow KBr + H$ has been studied by molecular beam techniques [Greene, Roberts & Ross (79)].

The atomic reactions yielding vibrationally excited products that have been studied recently are summarized in Table II. In a re-investigation of the reaction $O + NO_2 \rightarrow O_2^* + NO$, Basco & Norrish (43) have observed O_2^* vibrational levels as high as 11 (and perhaps 12) and the first, and possibly the second, vibrationally excited level of NO. Since the energy of the 11th level is equal to the exothermicity of the reaction, the authors believe that the results are in disagreement with the theory of Smith (41), which predicts a maximum value of vibrational energy corresponding to $v=8$. Of interest is the finding (43) that the electronic energy of the approaching atom can contribute to the vibrational energy of the product for the class of reactions



Using O atoms produced in an electrodeless discharge, Broida, Schiff & Sugden (83) obtained no evidence in the reactions $O + NO_2$ and $O + ClO_2$ for

the existence of vibrationally excited species. Various possibilities for the failure to observe O_2^* were considered, but the exact cause was not established.

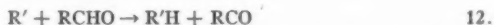
REACTIONS OF FREE RADICALS

Hydrogen atom abstractions.—Boddy & Steacie (84) have photolyzed 3-pentanone- d_{10} to obtain C_2D_5 radicals for the study of H-atom abstraction from $C(CH_3)_4$, $n-C_4H_{10}$, and *iso*- C_4H_{10} . The use of labeled radicals simplified the problem of analyzing the products. Their results, shown in Table III, indicate that the activation energies for the ethyl radical reactions are higher

TABLE III
H-ATOM ABSTRACTION FROM VARIOUS COMPOUNDS BY RADICALS

$R + R'H \rightarrow RH + R'$				a
$2R \rightarrow R_2$				b
R	R'H	$E_a - \frac{1}{2} E_b$ kcal./mole	$\log (A_a/A_b^{1/2})$ (A , cc./mole-sec.)	Investigators
C ₂ D ₅	C(CH ₃) ₄	12.6	4.55	Boddy, Steacie (84)
C ₂ D ₅	<i>n</i> -C ₄ H ₁₀	10.4	4.33	Boddy, Steacie (84)
C ₂ D ₅	<i>iso</i> -C ₄ H ₁₀	8.9	3.92	Boddy, Steacie (84)
C ₂ F ₅	H ₂	11.9	5.72	Price, Kutschke (85)
C ₂ F ₅	CH ₄	10.6	4.62	Price, Kutschke (85)
CF ₃	cycloC ₆ H ₁₂	5.0	4.76	Charles, Whittle (91)
C ₃ F ₇	cycloC ₆ H ₁₂	5.2	4.08	Pritchard, Miller (92)
CH ₃	H ₂ S	2.6(2.8)	4.68	Imai, Toyama (93, 94)

than those for methyl radicals. Price & Kutschke (85) have concluded that the order of ease of H-abstraction from a given substrate at 200°C. is $CF_3 > C_2F_5 > C_3F_7 > CH_3$. In studying the dependence of the rate of the reaction



upon the structure of the aldehyde, Birrell & Trotman-Dickenson (86) found that for $R' = CH_3$ and ($R = CH_3$; *n*- and *iso*- C_3H_7 ; *n*-, *iso*-, *sec*-, and *tert*- C_4H_9 ; allyl) the value of $\log k_{12}$ (cc./mole-sec. at 182°C.) was 8.25 ± 0.15 for all the aldehydes, but there was a variation in the Arrhenius parameters. For a different reaction (equation 12 with $R' = R = C_2H_5$) the activation energy was 5.9 kcal./mole and $\log (A$, cc./mole-sec.) was 11.1 and for $R' = R = n-C_4H_9$ the corresponding values for E and $\log A$ were 5.4 and 10.9, respectively [Kerr & Trotman-Dickenson (87, 88)]. Kozak & Gesser (89) concluded that methyl radicals abstract the hydrogen on the carbon atom in diethylamine, but the opposite interpretation, namely, that hydrogen atoms on nitrogen

are more labile than those on carbon, was proposed by Brinton (90) from his study of H-atom abstraction from amines.

There is a lack of agreement with respect to the activation energy for hydrogen abstraction by CH_3O radicals. Shaw & Trotman-Dickenson (95) studied the abstraction of hydrogen from a series of hydrocarbons by CH_3O radicals. The Arrhenius parameters showed some inconsistencies, but from a comparison of the behaviors of several radicals the authors suggested that the activation energy for H-atom abstraction from ethane by CH_3O should be about 9 kcal./mole. They felt that Wijnen's value (96) of about 4.5 kcal./mole for $\text{CH}_3\text{O} + \text{CH}_3\text{COOCH}_3$ may be too low. From a photolytic study Wijnen (97) derived an activation energy of 5.5 kcal./mole for $\text{C}_2\text{H}_5\text{O} + \text{C}_2\text{H}_5\text{COOC}_2\text{H}_5$. In the case of abstraction of a tertiary hydrogen from isobutane by $(\text{CH}_3)_3\text{CO}$ McMillan (98) has reported a value of 4 kcal./mole for the activation energy.

Other reactions of radicals with molecules.—Evidence for the occurrence of the reaction $\text{NH} + \text{NH}_3 \rightarrow \text{N}_2\text{H}_4$ has been obtained by Wannagat & Kohnen (99), who also have proposed that Rice's blue substance is $(\text{NH})_3$, the NH analog of O_3 . Rice & Luckenbach (100) have studied further the formation and reactions of NH. The type of reaction suggested as one step in the pyrolysis of *tert.*-butyl nitrite [Gray (101)]



has been found to occur in the gas phase at 180°C . [Jest & Phillips (102)] and in the liquid phase at 80°C . [Gray & Rathbone (103)]. Patsevich, Topchiev & Shtern (104) have discussed the reaction of C_2H_5 with NO_2 in terms of the processes



From their values of the ratio $(\text{RNO}_2)/(\text{RONO})$ that ranged from about 4 at -15° to 2.2 at 96°C . they concluded that the formation of RONO requires 1 kcal./mole more activation energy and has a steric factor approximately 1.7 times higher than the formation of RNO_2 . They reported that a reaction to form RO and NO did not occur under their conditions and that the ethyl nitrite molecule with excess energy is deactivated before it can decompose. On the other hand, Slagg, Rebbert & Ausloos (105) have observed that, in the photochemical decomposition of nitromethane, the reaction $\text{R} + \text{NO}_2 \rightarrow \text{RO} + \text{NO}$ is half as important as the formation of nitrite at 40°C . The ratio k_{14}/k_{15} for $\text{R} = \text{CH}_3$ was found to be 5 at 40°C . The reaction forming RO and NO has been suggested also as the explanation of the formation of nitric oxide during the gas phase nitration of methane by nitric acid [Schay & Giber (106)].

In the reaction of CF_3 radicals with aromatic hydrocarbons, Charles & Whittle (91) have found that addition to the ring rather than hydrogen abstraction is the main process. The addition reactions of methyl radicals

with acetylene, as well as hydrogen abstraction, have been studied by the use of deuterated reactants [Drew & Gordon (107)]. For the addition reactions, $C_2H_5 + C_2H_4 \rightarrow C_4H_9$ and $n-C_4H_9 + C_2H_4 \rightarrow C_6H_{13}$, the activation energies were determined as 8.6 and 7.3 kcal./mole and the values of $\log(A, \text{cc./mole-sec.})$ were 12.1 and 11.1, respectively [Kerr & Trotman-Dickenson (87, 88)].

Some of the papers (17, 18, 19) concerning the reactions of methylene radicals have been mentioned in an earlier section. Frey (108) has investigated the formation and decomposition of excited methylcyclobutane produced from cyclobutane by the addition of methylene from the photolyses of ketene and diazomethane. The data were interpreted on the basis that methylene can carry considerable excess energy. A report on the reaction of CH_2 with acetylene has appeared [Frey (109)]. The reactivity of methylene and the chemical evidence for its ground state have been considered in several publications (110, 111, 112). Diphenylmethylene has been observed to be less reactive in the gas phase than methylene (113).

Decomposition of radicals.—From the experimental data obtained in the photo-initiated chain decompositions of aldehydes activation energies for (a) $C_2H_5 \rightarrow C_2H_4 + H$, (b) $n-C_4H_9 \rightarrow C_2H_5 + C_2H_4$, and (c) $n-C_4H_9 \rightarrow CH_3 + C_3H_6$ have been estimated to be (a) 31.0, (b) 22.0, and (c) 27.1 kcal./mole [Kerr & Trotman-Dickenson (87, 88)]. As the authors mentioned, the values for the first two reactions are probably too low. With the first two activation energies and reasonable activation energies for the reverse reactions, one would obtain unlikely values for the endothermicities of the reactions (or for the bond dissociation energy of $R-H$). In a similar type of study reported earlier, Kerr & Trotman-Dickenson (114) derived an activation energy of 25.2 kcal./mole for the reaction $n-C_3H_7 \rightarrow CH_3 + C_2H_4$. This was lower than the value (34.9 kcal./mole) determined by Calvert & Sleppey (115) for n -propyl radicals produced in a different way. Later experimental findings of Kerr & Calvert (116) with propyl radicals from azo- n -propane at 0–300°C. give a value for the activation energy in good agreement with the result of Calvert & Sleppey. The discrepancies noted above for the high temperature photolyses of aldehydes indicate the difficulties that may be encountered in evaluating rates of elementary processes from systems involving a number of reactions.

Additional results have been obtained showing that the activation energy for the decomposition of an alkoxy radical into a methyl radical and a carbonyl compound is considerably smaller than that for the decomposition of an alkyl radical. The activation energy reported by Wijnen (97) for the decomposition of C_2H_5O is 13 kcal./mole, and that determined by McMillan (98) for the decomposition of $(CH_3)_2CO$ is approximately 11 kcal./mole.

Disproportionation and combination of radicals.—Most of the newly reported studies of radical reactions have given values for the disproportionation to combination ratio in a range that might have been anticipated from earlier work (see Table IV). The ratio for the reaction of $n-C_4H_9$ with $n-C_4H_9$, however, was found to be temperature-dependent corresponding to an activation energy difference of 1.3 kcal./mole (87). With partially deuterated

radicals the disproportionation to combination ratio at 25°C. has been evaluated at 0.15 for CH_3DCHD (13) and at 0.6 for $\text{CH}_3\text{CHDCHCH}_3$ (14). As in previous work, the ratio k_{16}/k_{17} is higher than one for a reaction involving an alkoxy radical (97). Pritchard & Dacey (118) have observed that reaction 18 has a temperature



dependence that can be expressed as 2.14 kcal./mole for E_{18} if each of the reactions, $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ and $\text{CH}_3 + \text{CF}_3 \rightarrow \text{CH}_3\text{CF}_3$, is assigned zero activation energy. Application of the transition state theory to these three

TABLE IV
RATIO OF DISPROPORTIONATION TO COMBINATION, k_{16}/k_{17}

R	CH_3	C_2H_5	C_2D_5	$n\text{-C}_4\text{H}_9$	$\text{C}_2\text{H}_5\text{O}$	$\text{R} + \text{R}' \rightarrow \text{RH} + \text{R}'(-\text{H})$
						$\text{R} + \text{R}' \rightarrow \text{RR}'$
						16.
						17.
R'	<i>iso</i> - C_3H_7 , 0.22* (117) (ref.)	C_2H_5 , 0.15 (88) (ref.)	C_2D_5 , 0.099 (84)' (ref.)	$n\text{-C}_4\text{H}_9$, 0.7† (87) (ref.)	$\text{C}_2\text{H}_5\text{O}$, 2.3 (97) (ref.)	
R'	<i>tert.</i> C_4H_9 , 0.7 (117) (ref.)	$\text{C}_2\text{H}_5\text{O}$, 1.3 (97) (ref.)				
R'	<i>tert.</i> C_4H_9 , 0.9 (98) (ref.)					

* "*iso*- C_3H_7 , 0.22" means that the ratio, k_{16}/k_{17} , for methyl (R) and isopropyl (R') is 0.22.

† at 100°C.

reactions gave good agreement between the calculated and experimental quantities (119). For radical combination reactions involving $n\text{-C}_4\text{H}_9$ (a) and $n\text{-C}_3\text{H}_7$ (b) the ratio $k_{ab}/(k_{aa}k_{bb})^{1/2}$ has been found to be 2.0 ± 0.2 , independent of temperature (87). Heller & Gordon (120) have studied the reaction of isopropyl radicals with deuterium atoms at 85°C., with particular regard to the subsequent reactions of the excited propane formed in the process.

THERMAL REACTIONS

First order reactions.—The results of rate studies on some of the reactions reported as first order are summarized in Table V and others will be discussed in the material that follows. Thermal reactions differ in complexity, and the portion of the process to which the first order classification applies will not be the same in all cases. The kinetic behavior may be based on the measurement of (a) an initial reaction yielding radicals or a radical plus an atom, (b) a molecular decomposition with no detectable radical or atomic intermediates and (c) an overall reaction involving several steps. For the decompositions of the first two substances shown in Table V the toluene carrier technique

was used and the activation energies were assigned to the dissociation energies of the $C_6H_5S-CH_3$ and $C_6H_5CH_2-COOH$ bonds (121, 122). The formation of ethylene from $CH_3COOCD_2CD_2H$ exhibits a hydrogen isotope effect that was determined by measurements of the C_2D_4/C_2D_3H ratio and found to be $(k_H/k_D) = 0.99 \exp(1145/RT)$ [Blades & Gilderson (124)]. In a comparison of the pyrolyses of $CH_3COOC_2H_5$ and $CH_3COOC_2D_5$, separate decompositions and decompositions of mixtures have been used to establish that the relative rate expression is $(k'_H/k'_D) = 0.8 \exp(1515/RT)$. The difference between this expression and that given above for the ethyl- d_4 acetate was attributed to secondary isotope effects (125).

TABLE V
FIRST ORDER THERMAL DECOMPOSITIONS

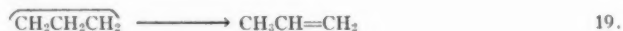
Substance	$\log(A, \text{sec.}^{-1})$	E kcal./mole	Investigators
$C_6H_5SCH_3$	14.48	60	Back, Sehon (121)
$C_6H_5CH_2COOH$	12.90	55	Back, Sehon (122)
$(C_6H_5)_2CHCOOH$	12.90	52*	Back, Sehon (123)
$CH_3COOC_2H_5$	12.59	48.0	Blades, Gilderson (125)
$CH_3COOC_2D_5$	12.68	49.5	Blades, Gilderson (125)
$C_2H_5COOC_2H_5$	12.72	48.5	Blades, Gilderson (126)
<i>n</i> - $C_8H_{11}Br$	13.09	50.5	Green, Maccoll, Thomas (132)
<i>n</i> - $C_8H_{13}Br$	13.13	50.5	Green, Maccoll, Thomas (132)
C_2H_5OOH	13.4	37.7	Kirk, Knox (133)
<i>iso</i> - C_3H_7OOH	15.2	40.0	Kirk, Knox (133)
<i>tert.</i> C_4H_9OOH	13.7	37.8	Kirk, Knox (133)

* Reaction is partly heterogeneous

Comparison of the rates of decomposition of cyclobutane 1,1,2,2- d_4 and cyclobutane gave the activation energy difference $E_D - E_H = 0.5$ kcal./mole and the ratio of frequency factors $(A_D/A_H) = 1.3$ [Srinivasan & Kellner (127)] Takahasi (128) has re-investigated the pyrolysis of toluene over a temperature range sufficient to cover the 738–864°C. region used by Szwarc (129) and the 860–945°C. region used by Blades, Blades & Steacie (130) from which discordant results (77.5 and 90 kcal./mole, respectively) were obtained for the activation energy. Szwarc had assigned his value to the bond dissociation energy $D(C_6H_5CH_2-H)$. In Takahasi's experiments the $\log k$ vs. $1/T$ plot was slightly curved. The results, although not completely consistent for different vessels, indicated that the apparent activation energy increases from about 74 to 104 kcal./mole with increasing temperature. In experiments at 830–955°C. with toluene labeled with a D atom in position 3 or 4 on the ring, the pyrolytic products contained H_2 , HD, a trace of D_2 , CH_4 , and CH_3D (131).

Formic acid has been reported to decompose homogeneously at 436–532°C. in two ways, neither of which is retarded by the usual chain inhibitors (134). Near 110°C. the *trans*-dimeric nitroso-alkanes undergo a first order gas phase reaction $(\text{RNO})_2 \rightarrow 2 \text{RNO}$, (135). The decomposition of CH_3NO at 360–449°C. in a flow system is partly heterogeneous and is markedly accelerated by added NO (136). The pyrolysis of $\text{Hg}(\text{CH}_3)_2$ has been studied in the presence of N_2 , C_2H_6 , and CH_3NNCH_3 (137). Barnard & Hughes (138, 139) have found that the pyrolyses of the C_2 and C_3 alcohols follow first order kinetics but are chain reactions. Other decompositions that have been studied are: $(\text{CH}_3)_3\text{CN}_2\text{C}(\text{CH}_3)_3$ (140), $(\text{CH}_3)_2\text{N}_4(\text{CH}_3)_2$ (141, 142), N_2O (143), and FCIO_3 (144). A method of treating pressure-time data to obtain the first order rate constant and the final pressure has been suggested (145).

A wealth of interesting data is becoming available as a result of studies of cyclopropane and its derivatives. The homogeneous isomerizations that have been observed for cyclopropane, methylcyclopropane [Chesick (20)], and 1,1-dimethylcyclopropane [Flowers & Frey (146)], at temperatures near 450–500°C. are:



In these investigations information about the rates of the individual reactions 20 to 24 has been obtained. With respect to energy transfer in the methylcyclopropane reaction, the efficiencies of inert gases on a collision basis are: He (.05), Ar (.17), H_2 (.07), N_2 (.23), CH_4 (.26), C_2H_6 (.44), butenes (1), toluene (.75). A comparison of the overall isomerizations of cyclopropane [Chambers & Kistiakowsky (147)], methylcyclopropane (20), and 1,1-dimethylcyclopropane (146) gives, for E : 65.0, 65.0, and 62.6 kcal./mole; for $\log(A, \text{sec}^{-1})$: 15.17, 15.45, and 15.05, respectively. In an experiment to test for the trimethylene biradical in reaction 19, by the addition of a large excess of ethylene, no positive evidence was obtained (148). For *cis*-1,2-dimethylcyclopropane the unimolecular geometrical isomerization to the *trans* isomer has been found to have $\log(A_\infty, \text{sec}^{-1}) = 15.25$ and $E = 59.4$ kcal./mole [Flowers & Frey (149)]. A slower structural isomerization to five-carbon olefins also occurs.

Second order reactions.—A summary of the rate data is given in Table VI.

For the reaction between nitric oxide and fluorine the observed rate has been assigned tentatively to the first step, $\text{NO} + \text{F}_2 \rightarrow \text{ONF} + \text{F}$, of the mechanism (151). The second order kinetics observed for the nitrogen dioxide-chlorine monoxide reaction have indicated that the reaction $\text{NO}_2 + \text{Cl}_2\text{O} \rightarrow \text{NO}_2\text{Cl} + \text{OCl}$ is the rate determining step (152). Ashmore & Spencer (153) have observed that the decomposition and formation of nitrosyl chloride occur not only by the molecular reaction, $2 \text{NOCl} \rightleftharpoons 2 \text{NO} + \text{Cl}_2$, but also by processes involving chlorine atoms in the gas phase and at the wall. For the mechanism of the HBr-catalyzed homogeneous decomposition of *tert.* $\text{C}_4\text{H}_9\text{OH}$ into water and isobutene, Maccoll & Stimson (155) considered one transition state involving a six-membered ring and another with a protonated oxygen

TABLE VI
SECOND ORDER THERMAL REACTIONS

Reaction	$\log(A, \text{cc./mole-sec.})$	E kcal./mole	Investigators
$\text{CF}_3\text{CH}_2\text{O}^\bullet\text{NO} + {}^{14}\text{NO}$	12.78	23.7	Kuhn, Günthard (150)
$\text{CH}_3\text{CH}_2\text{O}^\bullet\text{NO} + {}^{14}\text{NO}$	11.48	21.4	Kuhn, Günthard (150)
$\text{NO} + \text{F}_2$	11.78	1.5	Rapp, Johnston (151)
$\text{NO}_2 + \text{Cl}_2\text{O}$	10.64	11.6	Martin, Meise, Engelmann (152)
$\text{NO}_2 + \text{HCl}$	11.6	23.4	Rosser, Wise (154)
$\text{NO}_2 + \text{HBr}$	11.0	13.0	Rosser, Wise (154)
<i>tert.</i> $\text{C}_4\text{H}_9\text{OH} + \text{HBr}$	12.96	30.4	Maccoll, Stimson (155)
<i>tert.</i> $\text{C}_4\text{H}_9\text{OH} + \text{HCl}$	12.30	32.7	Lewis, Stimson (156)
<i>iso</i> - $\text{C}_3\text{H}_7\text{OH} + \text{HBr}$	12.00	33.2	Ross, Stimson (157)
<i>tert.</i> $\text{C}_5\text{H}_{11}\text{OH} + \text{HBr}$	12.01	27.1	Stimson, Watson (158)

on the alcohol accompanied by ion-pair formation. The thermal decomposition of ozone has been re-investigated by two research groups (65, 159).

Pyrolysis of aliphatic hydrocarbons.—By the use of new approaches, recent experimental and computer studies have provided new insight into the mechanism of the pyrolysis of ethane. Davis & Williamson (160) have used gas chromatography to examine the ethane reaction, especially the formation of minor products, in a flow system at 664–775°C. Skinner & Ball (161) have performed shock tube experiments at 784–1145°C. In these two investigations, as well as in the extensive computer study (162), the experimental data were interpreted essentially in terms of the Rice-Herzfeld chain mechanism. Davis & Williamson concluded that the observed pressure dependence of the reactions $\text{C}_2\text{H}_6 \rightarrow 2 \text{CH}_3$ and $\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H}$ tends to balance the effect of the half order kinetics resulting from chain termination by $(\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5)$, so that approximate first order behavior is observed for the overall reaction under certain conditions. In these studies the pyrolytic data could be fitted satisfactorily with A -factors and activation energies for the elementary steps in reasonable agreement with literature values obtained at much

lower temperatures. Determination of the rate constants by a computer technique gave a set of values that would predict experimental product distributions within 10 per cent, up to relatively high conversions over a temperature range 590–1100°C. for pressures near 1 atm. Snow *et al.* (162) regard some of the rate constants for elementary reactions calculated in this way from pyrolytic data as more accurate than previously determined values. Reports concerning the decompositions of methane (163) and ethylene (164) in shock wave experiments have appeared. Methyl radicals detectable by their ultraviolet absorption have been found when methane was pyrolyzed by the flash-heated grid technique (165).

Several publications have been devoted to a highly controversial aspect of the decompositions of hydrocarbons, i.e., the nature of the process occurring under conditions of maximum inhibition with nitric oxide or propylene. From measurements of the ($\text{CD}_3\text{H}/\text{CD}_4$) ratio of the products in the pyrolysis of mixtures of $n\text{-C}_4\text{H}_{10}$ and $n\text{-C}_4\text{D}_{10}$ with and without added NO at 430°C., it has been concluded that in the presence of NO not more than 2 per cent of the methane is formed by a non-chain process [Kuppermann & Larson (166)]. The subject of inhibition also involves the question of the importance of surface initiation and termination of radical chains. Voevodsky (167) has proposed that inhibitors destroy the active centers of the walls that are responsible for irreversible chain initiation, but do not affect the reversible processes of chain initiation and termination at the walls. From a study of the pyrolysis of butane Stepukhovich & Birger (168) have suggested that chains are generated on the walls, but the termination with propylene as inhibitor occurs homogeneously. Bryce & Ruzicka (169) have shown that allyl radicals can both add to double bonds and abstract hydrogen from hydrocarbons at 500°C. They advanced the idea that, in hydrocarbon decompositions fully inhibited by either propylene or nitric oxide, the residual reactions are short chain processes involving allyl-like radicals. For the fully inhibited decomposition of ethane, as well as other compounds, Wojciechowski & Laidler (170) have postulated a type of mechanism in which the inhibitor participates either directly or indirectly in both initiation and termination. The proposed reaction scheme for the inhibited ethane decomposition leads to first order kinetics and an overall activation energy close to the experimental values.

PHOTOCHEMISTRY

Direct photochemical reactions.—The publications appearing during the year indicate the likelihood of an increasing amount of research on the photochemistry of simple molecules. The following studies have been reported: (a) formation of hydrogen through the photolysis of H_2O vapor in the presence of oxygen (171), (b) photolysis of CO_2 (172), (c) development of a xenon-filled flash tube with high emission below 1650Å (173), (d) flash photolysis of CS_2 to produce vibrationally excited CS (174), and (e) photolysis of $^{15}\text{NH}_3$ in the presence of NO (175). Discussions of the mechanisms of the photolyses of NO_2 (176) and of O_3 (177, 178, 179) have been published.

Many of the results from photochemical studies involving organic molecules have been mentioned in earlier sections. Further work (180) on the photolysis of acetone has been directed toward ascertaining the importance of the reaction



Long (181) has suggested that the occurrence of reaction 25 may have produced misleading values of the activation energies for hydrogen abstraction by methyl radicals. From a study of the photolysis of CD_3COCD_3 at 198°C . with conversions up to 18 per cent, Henderson & Steacie (180) have shown that reaction 25 is not of significance when the decomposition of acetone is small. To account for some of the methane in the photolysis of acetone- d_6 -hydrogen mixtures, they postulated a reaction between methyl radicals and an excited molecule that contained both C—D and C—H bonds. Srinivasan & Noyes (182) have observed that illumination of CH_3COCH_3 and $^{18}\text{O}_2$ with 3130Å light gives $\text{CH}_3\text{C}^{18}\text{OCH}_3$ with a quantum yield of 0.45. Brown, Mitchell & Martin (183) have reported that from the photolysis of $^{14}\text{CH}_3\text{CO}^{14}\text{CH}_3$ and O_2 the resulting CO_2 is 90 per cent inactive and have suggested that the photo-oxidation does not give appreciable amounts of acetic acid.

From a study of the photo-oxidation of biacetyl at 4358Å, Porter (184) has concluded that the triplet molecules are formed with almost unit efficiency and the internal conversion of the singlet state is negligible. Dubois (185) has suggested a re-interpretation of the photolytic data on biacetyl. The photolyses of $\text{C}_2\text{F}_5\text{COC}_2\text{F}_5$ (186), $\text{CCl}_3\text{COCCL}_2$ (187), and $\text{ClCF}_2\text{COCF}_2\text{Cl}$ (188) have been investigated. In the flash photolysis of the last compound CF_2 radicals have been detected (189). When 5-hexen-2-one was subjected to 3130Å irradiation, the most important reaction was the formation of an isomer, presumably 1-methyl-2-oxabicyclo[2.2.0]hexane (190). With $\Phi_{\text{isom}} = 0.006$ and $\Phi_{\text{CO}} \leq 0.005$ at 139°C . it appears that this ketone with an isolated double bond has remarkable photochemical stability. The photodecomposition of cycloheptanone at 3130Å in the vapor phase at 70 – 100°C . is accompanied by a slightly more important photoisomerization ($\Phi = 0.14$ – 0.17) [Srinivasan (191)]



A re-investigation of the vapor-phase photolysis of azomethane from -47 to 50°C . has indicated that the curvature in the Arrhenius plot for methane formation below -10° is partially caused by a reaction between methyl radicals and azomethane adsorbed on the walls [Toby (192)]. Calvert, Thomas & Hanst (193) have studied the photolysis of mixtures of CH_3NNCH_3 and NO at 25°C . After a few minutes of irradiation the maximum concentration of CH_3NO is reached; the ratio $(\text{CH}_3\text{NO})/\text{P}_{\text{MgN}_2}^{1/2}$ is a constant for different azomethane pressures. In a continuation of the work on iodine excited by 1849Å radiation Gover & Willard (194) have observed that an electronically excited iodine molecule can react with hydrogen, methane, ethane, ethylene, and *n*-butane.

Photosensitized reactions.—Continued interest has been shown in reactions involving excited mercury atoms. The mercury-photosensitized decomposition of methylmercuric chloride vapor at 200°C. has been found to have a primary quantum yield of methyl radical formation of at least 0.95 and has been suggested as a new methyl radical source [Hirata, Sujishi & Gunning (1955)]. A study of the Hg 3P_1 photosensitized decomposition of H_2CO - D_2CO mixtures indicated that intramolecular elimination of hydrogen accounts for 40 per cent of the primary dissociation [Harrison & Lossing (196)]. Additional investigations of the mercury photosensitized reactions of methane (197), ethane (198), propane (198), and cyclohexane (199) have been carried out. With ethane and propane at 24°C., measurements at very low conversions showed that the hydrogen yield drops rapidly to a steady state value as the photolysis progresses [Back (198)]. This decrease, which occurs during the initial 0.05 per cent of the ethane reaction, is regarded as the result of the increase of ethylene until a steady state value is reached. Back (198) concluded that earlier work with ethane or propane that did not show this behavior was probably in the steady state region and gave quantum yields that were too low. The technique of monoisotopic mercury photosensitization has given evidence that a primary reaction between Hg $6(^3P_1)$ atoms and acetylene yields a mercury compound, presumably a mercury carbide (200). The results from a detailed study of the mercury photosensitized *cis-trans* isomerization of butene-2 are in agreement with an initial step yielding vibrationally excited molecules in the triplet state [Cundall & Palmer (201)].

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PROTEINS AND SYNTHETIC POLYPEPTIDES¹

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In recent years remarkable progress has been made towards the understanding of the architecture of the protein molecule. Chemical studies of amino acid composition and sequence led to the elucidation of the primary structure of molecules as complex as those of insulin (194), ACTH (149), glucagon (21), and lately of ribonuclease (115, 226) and the protein of the tobacco mosaic virus (4, 244). The chemical structure of the catalytic sites of some enzymes such as chymotrypsin (197), trypsin (62, 63), and phosphoglucomutase (137, 160) is gradually being unravelled. With the aid of x-ray techniques, three-dimensional analyses of sperm whale myoglobin (130, 131) and of horse oxyhemoglobin (182) were carried out employing the method of isomorphous replacement with heavy atoms. At 2 Å resolution Kendrew and his collaborators (131) were able to reconstruct the structure of myoglobin in almost atomic detail. The polypeptide chain fold, discovered first in the sperm whale myoglobin, has since been found in seal myoglobin (208) and in each of the four subunits constituting the hemoglobin molecule (182). New horizons are thus being opened for the precise description of the secondary and tertiary structures of proteins. The presence of the α -helix, first proposed for synthetic polypeptides and fibrous proteins by Pauling, Corey & Branson (175) has been established also in globular proteins. It is becoming evident, however, that many of the non-helical regions of globular protein molecules are by no means random in their arrangement. They may attain specific patterns characteristic of the particular individuality of the protein. Insight into the intricacies of the protein molecule was also gained through various physical chemical techniques such as measurements of optical rotatory dispersion (29), infrared and ultraviolet absorption (13), hydrogen-deuterium exchange (205), nuclear magnetic resonance (41), electric birefringence (138, 240), and by electron microscopy (246). The achievements reached by some of these methods will be discussed below. A recent modification of the equilibrium ultracentrifuge technique promises a convenient way for the molecular weight determination of proteins and polypeptides (269). Further progress in the elucidation of protein structure will undoubtedly pave the way for an understanding of the relation between structure and function of proteins and polypeptides on a molecular level. Such relations, when established, may explain the mechanical properties of fibrous proteins, shed new light on the molecular mechanism by which chemical energy is transferred into mechanical energy in muscle, clarify the details of the electrochemical behavior of globular proteins, elucidate the chemistry

¹ The survey of literature pertaining to this review was completed in December 1960.

of catalysis by enzymes, and lead to a better understanding of biological specificity in antibody antigen interactions as well as in many other biological processes.

The large amount of literature on proteins and polypeptides that has accumulated recently allows this review to cover a limited area only. Therefore, a few topics were chosen with which the reviewers were more closely acquainted and in which they had the opportunity to make their own contribution. Particular emphasis has been put on studies of the physical chemical properties of synthetic high molecular weight polypeptides, the poly- α -amino acids, in solution. The great value of these model compounds lies in their simplicity relative to the complexity of the natural proteins. Thus, by using such synthetic polypeptides, many physical, chemical, and biological properties can be studied in isolation, as it were. In view of the important progress made in the experimental field as well as in the theoretical understanding of the helix-random coil transition, a special section has been allotted to this topic. Finally, some of the progress made in elucidating the secondary and tertiary structure of proteins is reported. Several reviews dealing with topics related to those covered by the present article have appeared (127, 128, 146, 155, 204, 221).

POLY- α -AMINO ACIDS AS PROTEIN MODELS

Synthetic polypeptides of high molecular weight have continued to serve as important model compounds in the study of proteins. The investigation of their configuration in the solid state, using x-ray and infrared techniques, revealed that some of the poly- α -amino acids, such as poly- γ -methyl (or benzyl)-L-glutamate and poly-L-alanine, may exist in a helical configuration (the α -form) (13, 77). This structure closely resembles the α -helix suggested by Pauling & Corey (174, 175) for the secondary structure of proteins. The special helical configuration discovered in poly-L-proline (57) was used successfully in clarifying the structure of collagen (58, 186). Recent studies on the behavior of poly- α -amino acids in solution, using optical and hydrodynamic techniques, have shown that they may retain, in weakly interacting solvents, a definite secondary structure (146, 221) for which an intramolecularly hydrogen-bonded α -helical structure was postulated. In strongly interacting solvents the polymers exhibited a random form. Empirical and theoretical correlations between macromolecular configuration and optical rotatory properties and infrared absorption were established. These were used in attempts to clarify the secondary structure of proteins. Recent analyses of the physical chemical properties of different polyamino acids in solution indicate that the nature of the amino acid residues composing a synthetic polypeptide may have a marked effect on the nature of the helix formed—its stability as well as the sense of its twist. Finally, it is worth mentioning that the experimental and theoretical studies of the helix-random coil transitions of synthetic polyamino acids have already shed new light on the denaturation process in proteins. These attempts may lead in due course

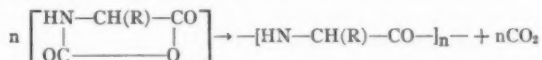
to a better understanding of the intra- and intermolecular forces prevailing in native proteins.

Most of the preparative methods developed during the last decade for the synthesis of polyamino acids use N-carboxy- α -amino acid anhydrides as monomers (125). As a rule, the polymerization is carried out in solution in the presence of suitable initiators. Polyamino acids thus consist, as do other synthetic polymers, of mixtures of homologous macromolecules of varying chain length. A large variety of amino acid polymers in a wide range of average molecular weights (10^3 to 10^6) have been prepared. These may be divided into the following groups: neutral polyamino acids with aliphatic or aromatic side chains, such as polyalanine and polyphenylalanine; acidic and basic ones, such as polyglutamic acid and polylysine; polyamino acids with imino peptide bonds, such as polyproline and polysarcosine; and those possessing special functional groups like polycysteine and polyserine. It is possible to prepare optically active polymers composed entirely of L or D amino acid residues, since the steric configuration of the amino acid monomer is retained during the polymerization. The polyamino acids most thoroughly investigated are those made of a single amino acid residue. It should be mentioned, however, that methods are available for the preparation of linear copolymers composed of several amino acids distributed at random along the polymer chain, as well as for the synthesis of multichain polymers and polypeptidyl-proteins. The large number of individual polyamino acids now available makes it possible to study their properties systematically.

A number of review articles dealing with poly- α -amino acids have been published recently. The synthesis and chemical properties of polyamino acids were summarized by Katchalski & Sela (125). The physical properties of synthetic polypeptides, particularly in the solid state, were discussed by Bamford *et al.* (13). Some of the properties of polyamino acids in solution were described by Shooter (221), Leach (146), and Blout (35). The earlier literature dealing with the physical chemical aspects of monomolecular layers at water/air and water/oil interface was reviewed by Cheesman & Davies (49). A summary of the biological properties of polyamino acids was given by Sela & Katchalski (217).

SYNTHESIS OF POLY- α -AMINO ACIDS

Mechanism and kinetics of polymerization of N-carboxy- α -amino acid anhydrides (NCAs).—The polymerization of N-carboxy- α -amino acid anhydrides (NCAs) proceeds according to the following scheme:



Primary, secondary, and tertiary amines, or strong bases such as sodium methoxide may be used as initiators when the polymerization is carried out in inert solvents (13, 125). Primary and secondary amines are most useful in the preparation of polypeptides with average degrees of polymerization, DP,

of 10 to 200, while tertiary amines and sodium methoxide were used for the preparation of high molecular weight polyamino acids with $DP > 200$.

The primary and secondary amine-initiated polymerization may be described in terms of an initiation reaction, a propagation reaction, and a termination reaction (126). Attack of the anhydride monomer by the amino group of the initiator leads to the opening of the ring, expulsion of a molecule of CO_2 , and the regeneration of an amino group. This in turn may attack a second molecule of anhydride and so on until the reaction ceases because of either the exhaustion of the monomer or the disappearance of terminal α -amino groups by a termination reaction. The mechanism and kinetics of the primary and secondary amine-initiated polymerization have been discussed by various authors (7, 10, 13, 112, 113, 116, 124, 125, 126, 157, 215, 220). The polymerization rates of various NCAs in different solvents have been tabulated by Katchalski & Sela (125).

A two-stage propagation reaction was observed by Doty, Blout, and their collaborators (46, 67, 116, 157) for the *n*-hexylamine initiated polymerization of γ -benzyl-L-glutamate-NCA in dioxane, ethylene dichloride, chloroform, or benzene. In dioxane, for example, the rate constant for the second propagation step was approximately five times larger than that for the first. Since the changeover from the slow to the fast propagation occurred when the average chain length had reached approximately eight residues, it was suggested as being caused by a configurational transition of the growing chains to the α -helical form. Two-stage propagation polymerizations with other NCAs have been reported (55, 157, 190, 257). The assumption that the polymerization rate is affected by the conformation of the growing chains was supported by the changes in optical rotation observed during the polymerization of D and L-N-carboxy- γ -benzyl glutamate anhydrides initiated by preformed L-polymer (157). The assumption was questioned by Ballard & Bamford (9 to 12; 68), who claimed that the increase in the rate of the propagation reaction should be related to the separation of the growing chains from the reaction mixture. Precipitation or gel formation is often observed when the polymerization of NCAs is carried out in solvents such as benzene, nitrobenzene, or dioxane. Furthermore, only one rate of propagation could be detected in dimethylformamide, a solvent in which polyamino acids form stable helices (157, 220). Theoretical analyses of the amine-initiated polymerization of NCAs have been reviewed previously (125). For a one-step propagation polymerization, in the absence of a termination reaction, a very sharp molecular weight distribution was predicted. Such a distribution was in fact found in samples of polysarcosine (80), poly- γ -benzyl-L-glutamate (103, 157), and poly- ϵ -carbobenzoxy-L-lysine (60). The case in which the propagation reaction exhibits two successive rates was recently analyzed theoretically (56). A method was suggested for the derivation, from kinetic data, of the transition chain length, and a broadening in the molecular weight distribution was predicted. However, the high ratio of weight average to number average degree of polymerization ($DP_w/DP_n = 8.5$) recorded for poly- γ -

benzyl-L-glutamate, obtained by a two-step propagation polymerization (161), exceeds that anticipated by the above theory.

The use of strong bases such as sodium methoxide and sodium hydroxide as initiators for the polymerization of NCAs in organic solvents was introduced by Blout and his collaborators (33, 34, 117). The polymerization initiated with these primers is fast, and the polymers that are formed have high average molecular weights. The strong base-initiated polymerization seems to be ionic in nature (116, 235). Propagation via anionic carbamates or anionic nitrogen was suggested (117). The data available, however, do not allow the precise formulation of the mechanism and kinetics of this important type of N-carboxy-amino acid anhydride polymerization.

Initiation of the polymerization of NCAs by tertiary amines such as pyridine or triethylamine has been widely used (8, 22, 27, 223, 258), and leads to polymers of rather high molecular weight. It proceeds most probably by an ionic mechanism (8, 260).

The techniques developed for the polymerization of NCAs permit the synthesis of copolymers of amino acids with a random sequence. In spite of the large number of such copolymers described in the literature [see Table IX in Katchalski & Sela (125)], only a few data are available on the kinetics of the copolymerization as well as on the amino acid residue distribution along the copolymer peptide chains formed. An analysis of the diethylamine-initiated copolymerization of the NCAs of ϵ -carbobenzoxy-L-lysine and γ -benzyl-L-glutamate in dimethylformamide revealed that the conversion rate in the copolymerization reaction is practically equal to the sum of the conversion rates of the individual monomers when polymerized singly, using the same amounts of solvent and initiator (220). From these results it was concluded that in the bimolecular propagation reaction only the monomers, and not the nature of the active ends of the growing chains, determine the copolymerization rate. It was thus possible to compute the compositional distribution along the copolymer chains, from the measured homopolymerization rates of the constituent NCAs.

Multichain polyamino acids and polypeptidyl-proteins.—The term "multichain polymer" denotes a branched polymer whose molecules are composed of linear polymeric chains attached to a polyfunctional core (196). Multichain polyamino acids have been obtained by the initiation of the polymerization of N-carboxyamino acid anhydrides with polyamines such as polylysine or polyornithine (214, 216, 218). Since no suitable organic solvents are available for these initiators, in most cases the polymerizations were performed in aqueous dioxane. A new polyfunctional initiator, consisting of a polylysine core and of short poly- β -benzylaspartate side chains, and which is soluble in organic solvent, has recently been prepared (268). It made possible the preparation of a great variety of multichain polyamino acids with sedimentation coefficients up to 11.5S. A general formula giving the size distribution of multichain molecules has been derived statistically (124). For multichain polyamino acids obtained in the absence of a termination reaction, a sharp

molecular weight distribution was predicted. Such a distribution was observed for many of the branched polyamino acids synthesized (268).

The polymerization of N-carboxyamino acid anhydrides in aqueous media using proteins as multifunctional initiators was described by Stahmann and his collaborators (16, 101, 136, 227, 245). Since the polymerization proceeds under mild conditions, polypeptidyl-proteins with distinct biological activity may be obtained. Polytyrosyl-trypsin (14) and polytyrosyl-chymotrypsin (224) have been synthesized and shown to retain full proteolytic activity in solution. Both modified enzymes could be covalently bound to water-insoluble resins via their polypeptidyl side chains. These resins are enzymatically active and retain their activity over prolonged periods. Polypeptidyl-gelatins containing additional aromatic amino acid residues unlike the parent protein, were found to possess marked antigenicity (6, 212, 213). Potentiometric titration and electrophoretic mobility of polypeptidyl-proteins were used to confirm the theory concerning the electrochemical behavior of native proteins (247, 248, 249).

CONFIGURATION OF POLY- α -AMINO ACIDS

Infrared and ultraviolet absorption spectra.—The infrared absorption spectrum ascribed to the amide bonds of polyamino acids is particularly sensitive to the conformation of the polypeptide backbone (13, 127). Synthetic polypeptides in the α -helix configuration are characterized by a C=O stretching vibration (amide I) with an absorption frequency of 1650 to 1660 cm^{-1} , a N—H deformation (amide II) with a frequency of 1540–1550 cm^{-1} and a N—H stretching with a frequency of 3290 to 3300 cm^{-1} . The corresponding frequencies for the β -structure are: 1630 cm^{-1} for the C=O stretching vibration, 1520 to 1525 cm^{-1} for the N—H deformation, and 3280 to 3300 cm^{-1} for the N—H stretching vibration. Stretching or rolling of polypeptide films often produces marked dichroism in the infrared absorption spectrum (13). When the polypeptide chains are in the α -form, the stretching modes of C=O and N—H show a dichroism parallel to the direction of rolling, while the N—H deformation mode shows a perpendicular dichroism. When the polypeptide chains are in the β -form, on the other hand, the dichroic behavior of the above bands is opposite to that of the α -form. These findings were explained by the assumption that the polypeptide chains align themselves in the direction of stretching or rolling and that the C=O and N—H bands are more or less parallel to the axes of the helices in the α -form, and are perpendicular to the direction of the stretched chains in the β -form. Some of the fibrillar proteins, e.g. keratin and silk, were found to exhibit in their α - and β -forms an infrared absorption and dichroism similar to that of the respective conformations of synthetic polypeptides (13, 127). Changes in the infrared absorption frequencies accompanying the denaturation of globular proteins were attributed to an $\alpha \rightarrow \beta$ transformation (1, 2, 51, 61).

The effect of side chains on polypeptide conformation in the solid state

was recently investigated by Blout *et al.* (30), using infrared techniques. Poly- γ -benzyl-L-glutamate, poly- β -benzyl-L-aspartate, poly- ϵ ,N-carbobenzoxy-L-lysine, poly-L-leucine, and poly-L-methionine exhibited the α -configuration in the films prepared. Poly-L-valine, poly-S-methyl-L-cysteine, and poly-L-serine, on the other hand, were shown to possess either the β - or a random structure. The non-helix-forming polypeptides seem to fall into two classes, those disubstituted on the β -carbon atom, and those having a heteroatom (oxygen or sulfur) attached directly to the β -carbon atom. An instrument for the detection of infrared dichroism in flowing polymer solutions has recently been described (28). With its aid it was possible to confirm the retention of the helical configuration of poly- γ -benzyl-L-glutamate and poly- ϵ ,N-carbobenzoxy-L-lysine in chloroform, and of poly-L-glutamic acid in a dioxane-water mixture. Polymer chains do not always orient parallel to the fiber axis. The alignment of short, extended synthetic polypeptide chains perpendicular to the fiber axis into a so-called "cross- β " structure has been investigated by Bradbury *et al.* (42). Films of poly- β -*n*-propyl-L-aspartate, when cast from warm dichloroacetic acid and orientated by stroking, showed C=O and N—H band frequencies characteristic of the extended β -configuration. From the infrared dichroism, however, it was concluded that the C=O and N—H bonds of the peptide group are orientated approximately along the direction of stroking. The x-ray diffraction pattern of the orientated films confirmed the interpretation given for the orientation of the polypeptide chains. A cross- β structure had been noticed previously in some proteins such as epidermin (192), fibrous insulin (3), and *Chrysopa* silk (173).

A thorough survey of the infrared spectra of some 40 different proteins has shown that the absorption frequency criteria developed for distinguishing between the α - and β -forms of polypeptides cannot be applied to all proteins (18). A similar conclusion was drawn by Elliott *et al.* (76) from their infrared absorption studies of water-soluble silk and lysozyme.

In view of the complexity of the infrared absorption spectra of proteins, the clarification of the vibrational modes responsible for the characteristic absorptions in low molecular weight model compounds is of considerable importance. A detailed analysis of the infrared spectra of acetylglycine N-methylamide and its N-deuterated derivative led to a complete assignment of the fundamental vibrational frequencies in the 1800 to 400 cm^{-1} region (167). Extending these studies to five other acetylamino acid N-methylamides (243) demonstrated the correlation between the absorption data and the folded and extended forms of these compounds. From the data obtained, a corrected conformation for polyglycine I and other polypeptides in the β -form was suggested. The Raman spectra of some peptides and of lysozyme were recorded by Garfinkel & Edsall (91).

An attempt to evaluate from theory the effect of macromolecular conformation on the amide I and amide II frequencies was made by Miyazawa (162). A perturbation treatment was applied in which intra- and interchain hydrogen bonding interactions were taken into consideration. Theoretical

studies were also made in partially orientated polymers on the correlation between infrared dichroism and distribution of chain direction (13, 17, 86, 87, 88).

Simple amides show a characteristic electronic absorption spectrum in the short ultraviolet region (185 to 210 $m\mu$) (104). Since the amide vibrational spectrum in the infrared region was found to be affected by macromolecular configuration, it could be expected that the amide ultraviolet absorption of polypeptides and proteins would similarly depend on the conformation of these molecules. Indeed, it was shown that the helix-random coil transition in poly-L-glutamic acid is accompanied by a marked increase in absorption at 190 $m\mu$ (118). From the change of the extinction coefficient ϵ_{190} with pH, it was possible, after correcting for the scattering effect and the ionization of the carboxyl side chains, to assess the helical content of the synthetic polypeptide as a function of pH. The values thus obtained were in good agreement with those derived from optical rotatory measurements (69). In view of the above, it is of interest to recall that Goldfarb (96) reported earlier that the optical density of protein solutions at 210 $m\mu$ increases on denaturation. Recently it was observed that a prominent absorption peak appears at 230 to 235 $m\mu$ when various proteins such as insulin, ribonuclease, papain, pepsin, and serum albumin are denatured (95). As it could be demonstrated that the aromatic amino acid residues do not account for the absorption changes noticed, it was concluded that the increase results primarily from a change in the environment of the peptide backbone. It still remains to be shown whether changes in protein configuration also affect the amide absorption at $\sim 190 m\mu$.

The overall shape of poly- α -amino acid molecules in solution.—Doty, Blout and their collaborators (65, 66) showed several years ago that the α -helix structure of poly- γ -benzyl-L-glutamate may be retained in solution. Measurements of viscosity, light scattering, and flow birefringence indicated that the polymeric molecules behave as rigid rods in weakly interacting solvents like chloroform, 2-chloroethanol, and dimethylformamide. Their length is proportional to the molecular weight, each amino acid residue contributing about 1.5 Å to the major axis. On the other hand, in strongly interacting solvents, such as dichloroacetic acid and trifluoroacetic acid, the polymer exhibits the properties of a random coil. The above conclusions have recently been corroborated by the finding (183, 265, 266) that the shear dependence of the intrinsic viscosity of poly- γ -benzyl-L-glutamate in *m*-cresol, a solvent favoring the α -helix conformation, is in complete accord with the viscosity theories developed for asymmetric rigid particles (134, 193, 202). It was thus possible to develop a new method for determining the rotatory diffusion constant θ , and thereby to derive the dimensions of the polypeptide molecules in solution. The rotatory diffusion coefficient of poly- γ -benzyl-L-glutamate in ethylene dichloride could also be derived from dynamic electrical birefringence measurements (239). From the value obtained, $\theta_{20,w} = 9.8 \times 10^8 \text{ sec}^{-1}$, for a polymer with an average molecular weight

of 350,000 a length of $2.7 \times 10^8 \text{ \AA}$ was obtained for the equivalent rigid rod or ellipsoid in good agreement with the value calculated, $2.4 \times 10^8 \text{ \AA}$, for an α -helix of the same molecular weight. Measurements of the dielectric properties of poly- γ -benzyl-L-glutamate in ethylene dichloride gave a linear relation between the dipole moment of the polypeptide and the average degree of polymerization, each amino acid residue contributing 3 to 4 Debye units along the helix axis (252 to 255). Good agreement was found between the times of relaxation calculated from dielectric dispersion measurements of different poly- γ -benzyl-L-glutamate samples and those expected for the corresponding α -helices. The study of the light scattering, viscosity, diffusion, sedimentation, and flow birefringence behavior, as well as of the optical rotatory dispersion of poly- ϵ ,N-carbobenzoxy-L-lysine in dimethylformamide solution, revealed that in solution the molecules of this polypeptide attain the form of a flexible imperfect helix (5, 60). The flexibility is most probably caused by short sequences of broken hydrogen bonds, which affect the shape of the molecule and thereby its hydrodynamic properties. These imperfections, however, do not reduce significantly the number of residues in the helical form and thus do not alter the optical rotatory behavior attributed to helical macromolecules (see section below). The study of the properties of different samples of poly-L-proline in solution also indicated that, although the hydrodynamic properties of this polymer are determined primarily by the end to end distance along the individual molecules, the optical rotatory properties are a reflection of the helical pattern of relatively short segments (10 to 15 prolyl residues). The ionization of high molecular weight poly- α ,L-glutamic acid in aqueous solution is accompanied by a marked increase in viscosity, reflecting a change in macromolecular conformation. In conjunction with the corresponding changes in other physical chemical properties it was suggested that a helix-random coil transition takes place (69, 97). It is of interest to note that no helical configuration could be detected in native poly- γ ,D-glutamic acid derived from *Bacillus anthracis* (74, 132, 187). Poly-L-lysine, in aqueous solution, resembles poly- α ,L-glutamic acid. It shows a typical polyelectrolyte behavior when ionized, and forms an α -helix on uncharging (5). Multichain polyamino acids resemble globular molecules more closely than linear ones in their hydrodynamic properties. For example, a multichain polymer containing 140 lysine residues in its backbone and about 14 γ -benzyl-L-glutamate residues in its side chains (average molecular weight of about 420,000) had a sedimentation constant in dimethylformamide as high as 1.5S but an intrinsic viscosity as low as $[\eta] = 0.3 \text{ dl./gm.}$ (268). Linear helical molecules with a similar molecular weight should give, in the same solvent, about $[\eta] = 20 \text{ dl./gm.}$ (65). Multichain polyamino acids therefore represent in many aspects good model compounds for the study of the hydrodynamic properties of globular proteins.

Optical rotation.—A theoretical analysis of the optical rotatory dispersion of polyamino acids in the helical configuration was given by Fitts & Kirkwood (81, 82, 83) and by Moffitt (163, 164). Both treatments were critically re-

viewed by Kauzmann (127). Equation 1, first derived by Moffitt (163), has been used extensively to interpret the optical rotatory dispersion data of synthetic polypeptides and proteins (29).

$$[R'] = \frac{a_0 \lambda_0^2}{\lambda^2 - \lambda_0^2} + \frac{b_0 \lambda_0^4}{(\lambda^2 - \lambda_0^2)^2} \quad 1.$$

In this equation $[R']$ is the mean residue rotation at wavelength λ , and a_0 , λ_0 , and b_0 are constants. The relation between $[R']$ and the specific optical rotation $[\alpha]$ is given by

$$[R'] = [\alpha](MRW/100)[3/(n^2 + 2)]$$

where MRW is the mean residue weight and n is the refractive index of the medium. For polypeptides in the right-handed α -helix configuration, a value of $b_0 \cong -600$ was calculated from molecular parameters (164); similarly, for a left-handed α -helix, $b_0 \cong +600$. For polypeptides in the random coil configuration, on the other hand, $b_0 = 0$ and Equation 1 reduces to the well-known one-term Drude expression. A revision of Equation 1 was later made by Moffitt *et al.* (165). It should be noted, however, that in the derivation of the above equations the effect of side chains was ignored and no allowance was made for contributions to the optical rotation by transitions at wavelengths other than those contributed by the peptide bond ($\lambda_0 \cong 200 \text{ m}\mu$). Kirkwood's polarizability theory for the average optical rotation (133) has been generalized recently by Tinoco & Woody (242) and used to calculate rigorously the optical rotatory dispersion of polyglycine and poly-L-alanine for light that is incident parallel and perpendicular to the helical axis. The expression obtained for the molar residue rotation contains six parameters, three of which should be the same for all α -helix polypeptides, while the other three are dependent on the nature of the polyamino acid. Comparing the expression obtained with that given by Moffitt (163) (Eq. 1) reveals that b_0 is a function of all the above six parameters; it is thus obvious that b_0 will not generally be a valid measure of either helix content or sense of helix.

Because of the large amount of data that had accumulated on the configuration of poly- γ -benzyl-L-glutamate in solution (see previous section), this polypeptide was among the first chosen for the experimental study of the effect of macromolecular conformation on optical rotatory properties (70, 166, 267). In its helical conformation poly- γ -benzyl-L-glutamate gave an "anomalous" optical rotatory dispersion that could be described by Equation 1, assuming $\lambda_0 = 212 \text{ m}\mu$ and $b_0 = -630$. For the random coil configuration, by contrast, $b_0 \cong 0$. The specific rotation at the sodium D-line was positive for the helical configuration ($[R']_D = 20$ degrees in chloroform) and negative for the random coil form ($[R']_D = -28$ degrees in dichloroacetic acid). In dichloroacetic acid-chloroform mixtures a remarkably sharp helix-coil transition occurred at a ratio of about 70:30 (v/v) (31, 267). In the case of poly- α ,L-glutamic acid, a polypeptide readily derived from poly- γ -benzyl- α ,L-glutamate, helix-coil transition could be effected in aqueous dioxane on

ionizing the γ -carboxyl side chains (69, 97).² The helical form ($[R']_D = -9$ degrees) gave an anomalous optical dispersion with $b_0 = -610$ and $\lambda_0 = 212$ $m\mu$. The random conformation ($[R']_D = -127$ degrees) showed a normal dispersion, i.e. $b_0 \approx 0$ (29). It should be noted that the $[R']_D$ values of the helical conformation of poly- α ,L-glutamic acid and of poly- γ -benzyl-L-glutamate are more positive by 50 to 100 degrees than those of the corresponding random coils. An analysis of the optical rotatory dispersion of a series of oligomeric γ -methyl-L-glutamate peptides, containing 3 to 11 amino acid residues per molecule, has recently been carried out by Goodman *et al.* (98, 99, 100). All of the synthesized oligopeptides, when studied in dichloroacetic acid, exhibited optical rotatory behavior characteristic for the random coil. In dimethylformamide, however, a considerable change was found in the values of $[\alpha]_D$ and b_0 on going from the hepta- to the nona-peptide. These changes were attributed to the folding of the peptide chain into the helical conformation.

The striking resemblance between the optical rotatory properties of some fibrous proteins and those of poly- γ -benzyl-L-glutamate and poly-L-glutamic acid (see section on proteins) stimulated a thorough study of the optical rotatory behavior of different proteins and polyamino acids. A behavior similar to that of the above polypeptides has been found for poly-L-alanine (75), poly-L-leucine (29), poly-L-methionine (181), poly- ϵ ,N-carbobenzoxy-L-lysine (5), and poly-L-lysine (5). The β -substituted polyamino acids [poly- β -benzyl-L-aspartate (12, 43, 123), poly-L-tryptophan (219), poly-L-tyrosine (56), poly-1-benzyl-L-histidine (171), and poly-L-serine (39, 78)], however, showed an entirely different optical rotatory behavior. Therefore, the proximity of side-chain substituents to the polypeptide backbone seems to affect macromolecular configuration and optical rotatory behavior. The helix-random coil transformation of poly- β -benzyl-L-aspartate in chloroform-dichloroacetic acid mixtures is accompanied by a large change in rotation in a direction opposite to that recorded for poly- γ -benzyl-L-glutamate (123). Furthermore, the optical rotatory dispersion of poly- β -benzyl-L-aspartate in its helical conformation could be described by Moffitt's equation assuming a positive b_0 of $+630$ ($\lambda_0 = 212$ $m\mu$) in a range of wavelengths where poly- γ -benzyl-L-glutamate shows a negative b_0 of -630 (123). In view of these observations it was suggested that the helices of poly- β -benzyl-L-aspartate and poly- γ -benzyl-L-glutamate are of opposite senses of twist. A left-handed helix was ascribed to the former polypeptide and a right-handed helix to the latter. The suggestion was supported by the regular variation of optical rotatory properties with the composition of copolymers of β -benzyl-

² For the poly- γ ,D-glutamic acid derived from *Bacillus anthracis*, a linear dependence was obtained between the degree of α -carboxyl ionization (20 to 100 per cent) and the corresponding values of $[\alpha]$ at 400 $m\mu$ (74). It was thus concluded that the changes observed in $[\alpha]$ are exclusively due to ionization of the carboxyl groups closely attached to the asymmetric carbon atoms and do not involve conformational changes in the γ -polypeptide backbone.

D-aspartate and γ -benzyl-L-glutamate (12, 123). The optical rotatory behavior of poly-L-tryptophan (219) was recently found to resemble that of poly- β -benzyl-L-aspartate. The configurational change that occurs when dichloroacetic acid is added to solutions of the polymer in dimethylformamide is accompanied by an increase in $[\alpha]_D$, and the solution in dimethylformamide gives a positive value for b_0 of +410 degrees (for $\lambda_0 = 212 \text{ m}\mu$). A complicated rotatory behavior was found in the case of poly-1-benzyl-L-histidine (171). The variation of the specific rotation with the dichloroacetic acid content in chloroform indicated the existence of three distinct configurations: Form I exists in chloroform and is characterized by $[\alpha]_{546} = +25$ degrees; Form II ($[\alpha]_{546} = -208$ degrees) is obtained on neutralization of the imidazole side chains with an equivalent amount of dichloroacetic acid; Form III ($[\alpha]_{546} = +28$ degrees) appears in pure dichloroacetic acid. On the basis of the infrared absorption and dichroism it was concluded that Form II consists of peptide chains in the helical configuration. The onset of a positive Cotton effect around 240 to 250 $\text{m}\mu$ for polybenzyl-histidine II, similar to that recorded for poly- β -benzyl-L-aspartate, further suggested that both polypeptides have the same sense of twist in their helical configuration. The difficulty in deriving macromolecular structures from optical rotatory studies, alone, may be exemplified by poly-L-tyrosine (56). The sharp decrease in dextrarotation that occurs on ionization in aqueous solution or on the adding of excess dichloroacetic acid to the polypeptide solutions in dimethylformamide suggests a helix-coil transition similar to that recorded for poly- γ -benzyl-L-glutamate or for poly-L-glutamic acid. The occurrence of such a transition has been suggested by hydrodynamic data (56). Both the helix- and the random-coil configurations of poly-L-tyrosine, however, show an anomalous dispersion with $b_0 \cong +500$. In this connection it is pertinent to note that even L-tyrosine gives an optical rotatory dispersion that cannot be fitted by a one-term Drude equation (201). It was the unusual behavior of poly-L-tyrosine that led Downie, Elliott & Hanby (71) to the unlikely suggestion that poly-L-tyrosine does not form a helical configuration even in solvents of low hydrogen-bonding capacity. In aqueous solution poly-L-serine exists in the random conformation (78).³ Poly-O-acetyl-L-serine, on the other hand, has been shown by infrared analysis to possess a β -extended structure in chloroform and a random-coil conformation in dichloroacetic acid (78). The rotatory dispersion of both forms may be described by a one-term Drude equation (Eq. 5). The former structure is characterized by $[\alpha]_{546} \cong +130$ degrees and a dispersion constant $\lambda_c \cong 215 \text{ m}\mu$, while the latter gives $[\alpha]_{546} \cong +30$ degrees and $\lambda_c \cong 120 \text{ m}\mu$. The fact that the β -random-coil transformation is accompanied by a change in optical rotation of approximately 100 degrees and of λ_c of about 100 $\text{m}\mu$ is surprising, and a theoretical investigation of these facts seems desirable.

³ Some doubts have been raised recently as to the optical purity of the poly-L-serine investigated, since the alkaline treatment applied in the deacetylation of poly-O-acetyl-L-serine was found to cause partial racemization (39).

Some of the physical and chemical properties of collagen and gelatin have been correlated with the presence of proline and hydroxyproline, in relatively large amounts, in these proteins (45, 102, 184, 185). The study of the properties and configuration of amino acid polymers containing proline and hydroxyproline is therefore of interest. The x-ray analysis of orientated films of poly-L-proline has shown a similarity in structure between natural and synthetic high molecular weight compounds (57, 58, 186, 189, 195). Proline, because it is an imino acid, when linked in a peptide group can only contribute strongly to hydrogen-bonded structures through its C=O group, since the nitrogen of the prolyl residue carries no hydrogen. Furthermore, as a result of the cyclic imino group, there is no free rotation between the imino group and the α -carbon. This in turn limits the configurational possibilities of proline-containing proteins and polypeptides.

Kurtz *et al.* (140) have demonstrated that poly-L-proline can exist in two forms exhibiting markedly different optical rotations. If the polymer is precipitated from the polymerization medium (pyridine) and redissolved in acetic acid, its initial specific rotation $[\alpha]_D^{25}$ is +50 degrees. This material has been denoted Form I (32, 108). On standing at room temperature, however, the acetic acid solution slowly changes in rotation over a period of several days and reaches a final value of $[\alpha]_D^{25}$ -540 degrees (140, 141). The polyproline having this specific rotation has been denoted Form II. A number of other solvents such as formic acid and benzyl alcohol also favor the forward mutarotation of Form I into Form II. Reverse mutarotation of Form II into Form I could be effected in solvent mixtures such as acetic acid-*n*-propanol (1:9 *v/v*) (228). Generally, good solvents favor the formation of Form II, while poor solvents stabilize Form I. Since this cyclic process of mutarotation could be repeated indefinitely, it was concluded that the variations in specific optical rotation reflect configurational transitions in the individual polymer molecules. A study of the optical activity of racemic multichain polyamino acids bearing short poly-L-proline side chains revealed (268) that the mutarotation of the type described above occurs only when the average degree of polymerization exceeds four to six. It has been suggested that the transitions between the two forms of poly-L-proline stem from a series of *cis-trans* isomerizations at the peptide bonds of the polymer (140). An x-ray analysis of poly-L-proline II has shown that the polypeptide molecules in this form have a configuration of a left-handed helix possessing three proline residues per turn, with a residue repeat of 3.12Å along the longitudinal axis (57). A *trans* configuration was attributed to all imide bonds in Form II. The structure of poly-L-proline I has not as yet been elucidated by x-ray analysis. Indirect evidence derived from an investigation of the mechanism of mutarotation, however, indicates that Form I in solution is probably a right-handed helix with all peptide bonds in the *cis* configuration (229). Poly-L-proline chains constructed from atom models show that such a right-handed helix may be built and that it contains $3\frac{1}{2}$ residues per turn and has a unit translational repeat distance of 1.85Å (108).

When the kinetics of the forward and the reverse mutarotations were studied at different polymer concentrations, it was found that the rate of change in optical rotation at any given $[\alpha]$ was directly proportional to polymer concentration. On the other hand, the change, with time, in optical rotation during any single experiment could not be described in all cases as a first order reaction (72, 229). This is explicable either by lack of proportionality between the change in optical rotation and the corresponding change in the number of peptide bonds that underwent transformation (72), or by a change in the ease with which the various peptide bonds undergo a *cis-trans* isomerization during the progress of the mutarotation reaction (229). That the change of $[\alpha]$ with time proceeds in various solvents according to different orders of reaction seems to support the latter assumption. An analysis of the kinetics of mutarotation led to a general formula describing the intramolecular *cis-trans* isomerizations along the macromolecular chain (229). From the temperature dependence of the rate of the forward mutarotation in acetic acid and of the reverse mutarotation in acetic acid-*n*-propanol (1:9 v/v), an enthalpy of activation of about $\Delta H^* = 20$ kcal. per mole of prolyl residue was calculated for both reactions. This value is in agreement with the assumption that the basic process underlying the mutarotation of poly-L-proline is the unlocking of the planar peptide bond, leading to a *cis-trans* isomerization (176). Evidence for the occurrence of the *cis-trans* isomerization was also provided by the catalysis of the forward and reverse mutarotations by small amounts of strong acids (229). Since strong mineral acids were shown to combine with the imino peptide bonds of poly-L-proline and poly-O-acetyl-hydroxy-L-proline, the catalytic effect was explained by assuming that proton binding to the imide nitrogen destroys the double bond character of the peptide bonds, thus facilitating the *cis-trans* isomerization. An analogous mechanism was suggested to explain the onset of free rotation around the amide bond of N,N-dimethylacetamide, detected by nuclear magnetic resonance techniques, on acidifying its aqueous solutions (24).

The specific levorotations and viscosities of poly-L-proline II solutions in concentrated aqueous lithium bromide are considerably lower than those in water. The neutral salt therefore seems to cause destruction of the asymmetric macromolecular configuration of Form II (108). Experimental evidence was advanced to indicate that the collapse in structure in this case does not arise from *trans-cis* isomerization at the peptide bonds but probably involves a *trans'-cis'* isomerization at the α -carbon-carbonyl carbon bond. Poly-L-proline chain models show a definite restriction to rotation about this bond.

Poly-O-acetyl hydroxy-L-proline and poly-O-tosyl hydroxy-L-proline show both forward and reverse mutarotations, similar to those of poly-L-proline (142). The kinetics of the forward mutarotation of poly-O-acetyl hydroxy-L-proline in formic acid and of the reverse mutarotation in dimethylformamide were recently investigated (73). The forward and the reverse mutarotations were found to have activation energies of about 23 kcal. per

mole. Until now no mutarotation could be detected for polyhydroxy-L-proline.

Polyamino acids in their random configuration do not possess macro-molecular asymmetry. It might have been assumed, therefore, that the molar residue rotation of randomly coiled homo-polyamino acids was identical with that of the corresponding low molecular weight amino acid derivatives. This does not seem to hold, however, in most of the cases tested. For example, the molar residue rotation of poly-L-tryptophan in dichloroacetic acid-dimethyl-formamide (4:1 v/v) is $[R']_{546} = +420$ degrees, while that of benzyloxycarbonyl-L-tryptophan hydrazide in the same solvent system (219) is $[R']_{546} = -52.3$ degrees. Similarly, the optical rotation of poly-L-methionine is $[R']_{546} = -106$ degrees, while that of benzyloxycarbonyl-L-methionine amide is $[R']_{546} = -28$ degrees, both measured in trifluoroacetic acid (181).

The optical rotatory dispersion data both for polyamino acids and for proteins, accumulated over recent years, clearly illustrate the theoretical and experimental difficulties involved in correlating optical rotation with asymmetric macromolecular structure. It is believed, however, that the optical rotatory tool has not been fully utilized as yet. An analysis of the Cotton effect in the region of the optically active absorption bands (139, 168), an evaluation of the circular dichroism (139, 168), and the estimation of the optical rotation along the different axes of the molecule (238 to 242) may shed new light on the configuration of the polypeptide chain as well as on the polarizabilities and the internal interactions between the different groups making up the molecule. Some encouraging results in these directions have already been obtained. The onset of a Cotton effect at 260 m μ was detected for poly- β -benzyl-L-aspartate (123) and for poly-1-benzyl-L-histidine (171). The complexing of helical poly-L-glutamic acid with acriflavine induced a marked Cotton effect in the vicinity of the absorption band of the dye (35). Rotatory dispersion measurements, of partially orientated poly- γ -benzyl-L-glutamate molecules in an externally applied electric field, led to the evaluation of the specific rotations parallel and perpendicular to the helix of the polypeptide (240).

THEORY OF HELIX-COIL TRANSITION

The discovery of a helix-coil transition in synthetic poly- α -amino acids prompted various investigators to analyse this phenomenon theoretically. Such analyses are of great importance in understanding the structure and stability of protein molecules (178, 179, 198, 199, 272).

The thermodynamic stability of a polypeptide chain in a completely α -helical configuration, as compared with that of a completely non-hydrogen-bonded random coil, was investigated by Schellman (198). The helical configuration is obviously characterized by a low enthalpy and low entropy as compared with the corresponding random coil. A calculation of the free energy of unfolding per mole polypeptide yielded the relation:

$$\Delta F_{(\text{unfolding})} = (n - 4)\Delta H_{\text{res}} - (n - 1)T\Delta S_{\text{res}} \quad 2.$$

where n denotes the number of residues per molecule, ΔH_{res} is the change in enthalpy on breaking one mole of peptide hydrogen bonds, and ΔS_{res} is the change in entropy accompanying the unlocking of one mole of amino acid residue from the constraint of the helix. The coefficients $(n-4)$ and $(n-1)$ give the total number of hydrogen bonds present and amino acid residues locked in the helical structure, respectively. From the heat of dilution of aqueous urea solutions it was possible to estimate $\Delta H_{\text{res}} = 1.5$ kcal. Considerably higher values (4 to 6 kcal.), however, were recorded by other authors (144, 156, 234). Configurational considerations led to an approximate value of $\Delta S_{\text{res}} = 3$ to 4 e.u. The numerical values quoted ignore the contribution of the peptide side chains to both the enthalpy and the entropy of unfolding. The values of ΔS_{res} and ΔH_{res} recorded by Schellman (198) show that the free energy of unfolding ΔF_{unfold} is negative at room temperature for n smaller than 8 to 15. Short peptide chains are therefore unstable in the helical configuration. By means of Equation 2 it is also possible to estimate, as a function of chain length, the temperature range in which the helix-coil transition occurs. The higher the molecular weight of the polypeptide, the narrower its temperature transition range. The original "all or none" model (198) was later refined by allowing partial unwinding at the edges of the helix (199). Discontinuities in the helical region, however, were assumed to be improbable. The probability P_m for the formation of m adjacent hydrogen bonds in a molecule of a chain length n was given by the expression

$$P_m = 1/Q(n-3-m)e^{m\Delta F_{\text{res}}/RT}e^{-3\Delta S_{\text{res}}/R} \quad 3.$$

where $\Delta F_{\text{res}} = \Delta H_{\text{res}} - T\Delta S_{\text{res}}$ and Q is a normalization factor. The completely random state, in which $m=0$, was taken as the reference state; therefore its probability is $P_0 = 1/Q$. The factor $(n-3-m)$ gives the number of positions in the chain into which m consecutive hydrogen bonds can be located. The factor $e^{-3\Delta S_{\text{res}}/R}$ arises because upon formation of a helical segment, the number of residues locked into the helix is greater by three than the number of hydrogen bonds formed. From Equation 3 it could be deduced that, for high values of average hydrogen bonding $\langle m \rangle$, most of the molecules wind up into helices, which are slightly unwound at their edges. A decrease in $\langle m \rangle$ is not accompanied by the formation of intermediate structures possessing short helical segments, but leads mainly to an increase in the fraction of molecules having a completely random configuration. A plot of $\langle m \rangle$ versus temperature demonstrated a lack of symmetry in the transition, which was missed in the "all or none" treatment. The fluctuation of the helical segment along the polypeptide molecule was further shown to stabilize the helical state and to broaden the temperature range of the transition.

In contradistinction to the previously described treatment, Peller (177, 178) proposed a model in which helical and non-helical segments might alternate along the polypeptide chain. This treatment is particularly valuable for long chains. A specific contribution to the free energy of the chain was attributed to the junctions between the helical and the random coil segments.

An Ising partition function Δ was employed to describe the range of configurational states possible [see also (188)].

$$\Delta = \sum_{(N_h, N_c, N_{hc})} g(N_h, N_c, N_{hc}) (j_h)^{N_h} (j_c)^{N_c} (Y_{hc})^{N_{hc}} \quad 4.$$

In this equation $g(N_h, N_c, N_{hc})$ is the number of ways of constructing a chain from N_h helical units, N_c non-helical units, and N_{hc} junctions between helical and non-helical regions. A unit was assumed to consist of three amino acid residues; j_h and j_c are the internal partition functions for the helical and random coiling units. Y_{hc} is the partition function for the correction attributable to the end effects that occur at each helix-coil junction, and it expresses the likelihood of junctions between helical and coil regions. From the partition function it was possible to calculate the helix-coil transition as a function of temperature. The sharpness of the transition was found to depend on the value of Y_{hc} ; the smaller Y_{hc} , the sharper the transition. From a theoretical estimate of Y_{hc} it was deduced that sharp transitions are to be expected for long polypeptides and that chains possessing an appreciable number of junctions appear mainly during the helix-coil transition. It is of interest to note that a calculation of the logarithm of the ratio R between the number of helical and non-helical residues gives a function that does not vary linearly with $1/T$. Differentiation of $\ln R$ with T , in the neighborhood of the transition temperature gives an apparent enthalpy $\Delta H^* = RT^2 d \ln R / dT = 3\Delta H_{res} / Y_{hc}$. Since Y_{hc} is considerably smaller than unity, $\Delta H^* \gg \Delta H_{res}$. Thus it was suggested that the large heats and entropies, characteristic of reversible protein denaturation as well as of polypeptide transitions, might be better associated with small values of a parameter such as Y_{hc} , rather than with a certain large number of hydrogen bonds being severed in an "all or none" manner.

An interesting method for the handling of the partition function used to describe the helix-coil transition in terms of the eigenvalues and eigenvectors of a characteristic matrix has recently been described by Zimm & Bragg (270, 271). In the model adopted to describe hydrogen-bonding in polypeptides, in analogy with the previous models discussed, it was assumed that bonding is allowed only between a group and the third preceding it. Two principal parameters were introduced: a statistical parameter s , which is essentially an equilibrium constant for the bonding of segments to a portion of the chain, already in helical form; and a special correction factor σ for the initiation of a helix. The parameters s and σ play the same role as the quantities j_c/j_h and Y_{hc}^2 , which appear in the treatment of Peller (177, 178). The sharpness of the transition was found to depend on the initiation parameter, as in the treatment given by Peller. The conclusions about the dominant configurations that prevailed under various conditions were illustrated by Zimm & Bragg (271) in an illuminating diagram that demonstrated the stability of the various configurations as a function of both the chain length n and the statistical parameter s . Polypeptides of any chain length attain a random configuration at low values of s . Molecules with low degrees of polymerization but high values of s exist as single helices with occasional

disorder at the ends. The dominant configuration for long chains that possess high values of s consists of helices with scattered random sections and terminal disorder. Randomness prevails, however, for any value of s when the chain length is below a critical value. The numerical values of s and σ may be derived from a study of the helix-coil transition, with temperature, of a sequence of polymers having different chain lengths. Such a study has been carried out for the case of poly- γ -benzyl-L-glutamate in dichloroacetic acid-ethylene dichloride mixtures (271, 272).

The evaluation of the complete partition function for the polypeptide backbone, with the aid of either the method of Lagrangian multipliers or the method of steepest descents, was described by Gibbs & DiMarzio (93, 94). The internal rotation angles were used as variables for the evaluation of the configurational partition function by Lifson & Roig (150). As in the case of Zimm & Bragg (271), a matrix representation of the partition function was applied. The type of calculation that was employed led to a rigorous treatment of the phenomenon of helix-coil transition in polypeptide molecules. Explicit formulae were derived for the degree of intramolecular hydrogen-bonding, average number of helical sequences, and distribution of their lengths. These may be of value in the understanding of the hydrodynamic behavior of polypeptides at and above the transition region (169).

The influence of solvent composition on the helix-coil transition was discussed in detail by a number of authors (94, 179, 198, 199). Preferential binding of one of the components, e.g. urea, to the random chain will favor the formation of the random configuration and will usually lower the helix-coil transition temperature. The free energy of combination ΔF_b with the random fragments of the polypeptide could be expressed by $\Delta F_b = -MRT \ln(1 + Ka)$ (179, 198, 199); where M is the number of combining sites, K is the intrinsic equilibrium constant, and a is the activity of the combining small molecules in the solution. A sharp transition in macromolecular conformation, with change in solvent composition, was recorded for various polyamino acids. Such a transition was found for poly- γ -benzyl-L-glutamate (31) and poly- β -benzyl-L-aspartate (123) in chloroform-dichloroacetic acid mixtures, for poly- ϵ ,N-carbobenzoxy-L-lysine (5) and poly-L-tryptophan (219) in dimethylformamide-dichloroacetic acid mixtures, and for poly-L-methionine (181) in chloroform-trifluoroacetic acid mixtures. In some cases the preferential binding of the solvent to molecules in the random configuration is accompanied by a considerable decrease in enthalpy and entropy. In such systems a solution of molecules possessing a random structure may have a lower enthalpy and entropy than a solution of the same molecules possessing a helical structure. The helical structure under these circumstances will be the more stable one at elevated temperatures. Such "inverted transitions" were recorded for proteins and synthetic polypeptides (70, 84, 119). The effect of electrostatic charge on helix stability has been investigated (179, 198). Electrostatic repulsion forces that prevail in polypeptides, such as clupein, polylysine, and polyglutamic acid, reduced the stability of folded forms. Furthermore, it could be

predicted (179) that any electrostatically induced structural transition would be accompanied by an ionization that would result in a net charge increase.

The problems encountered in protein research of configuration stability and configurational change are obviously considerably more complex than those of simple polypeptides. It is generally accepted, however, that the considerations described above can be applied to the elucidation of the configurational changes taking place in proteins in the presence of denaturing agents, on ionization, or at elevated temperatures.

SECONDARY AND TERTIARY STRUCTURE IN PROTEINS

According to Linderström-Lang (151), the structure of a protein can be examined at three different levels that correspond to the primary, secondary, and tertiary structure. He defined as primary structure the sequence of the amino acid residues in the polypeptide chain or chains, as secondary structure the way in which the backbone of the polypeptide chains is folded or coiled, and as tertiary structure the way in which the folded or coiled polypeptide chains are themselves arranged in space and packed into the protein molecule. The secondary structure arises from hydrogen-bonding of the C=O and N—H groups of the peptide backbone. The tertiary structure stems from factors such as interchain hydrogen bonds, salt linkages, and hydrophobic bonds. Since the possibility of a three-dimensional mapping of all the atoms in a protein molecule by standard x-ray techniques is still remote, physical and chemical methods aimed at obtaining partial information concerning the secondary and tertiary structure have been developed. The results obtained with some of these methods will be given below. By correlating such pieces of information it may be possible to arrive at a hypothetical model for a given protein. An interesting attempt in this direction was recently made by Scheraga, who suggested a tentative model for ribonuclease (206).

SECONDARY STRUCTURE

Optical rotation.—In parallel to the investigations on the optical rotatory behavior of synthetic polypeptides, a considerable amount of work has been carried out recently on the optical rotation of proteins. Fibrous proteins such as myosin, paramyosin, tropomyosin, and light meromyosin, in aqueous solution, exhibit an anomalous rotatory dispersion that could be described by the Moffitt equation (Eq. 1) assuming $b_0 \cong -400$ to -600 and $\lambda_0 = 212$ μ (53, 54, 129). The values obtained for b_0 were taken as a measure of helix content, using poly- γ -benzyl-L-glutamate as a reference model compound ($b_0 \cong -630$, $\lambda_0 = 212$ μ for the 100 per cent helical conformation). As expected, upon denaturation a drop to approximately zero was observed for the value of b_0 . Among the fibrous proteins collagen is unusual because it shows not only a marked drop in levorotation (-350° to -110° in ichthyocol) upon denaturation (transformation into gelatin), but also a simple dispersion [$\lambda_c \cong 205$ μ (see Eq. 5)] both in the native and the denatured states

(38, 52, 79). Fibers of collagen do not possess an α -helix conformation but consist of polypeptides in the poly-L-proline II configuration (57, 229) twisted into a triple helix (58, 186, 189). As a rule, globular proteins in aqueous solution exhibit a normal optical rotatory dispersion that can be described by a one-term Drude equation. In solvents of low hydrogen bonding capacity an anomalous dispersion might appear, however, most likely as a result of an increase in helix content. Such an anomalous dispersion has been observed in 2-chloroethanol solutions of bovine serum albumin, ovalbumin, ribonuclease, and histone (64, 256).

The helix configuration is believed to be an important structural element in globular proteins; the dispersion of such proteins in aqueous solution, however, is invariably simple (see Eq. 5).

$$[R'] = \frac{K}{\lambda^2 - \lambda_c^2} \quad 5.$$

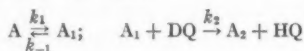
In this equation K and λ_c are constants, the latter being denoted the dispersion constant. Yang & Doty (267) have shown that when λ_c varies in the range of 212 $m\mu$ to 255 $m\mu$, the experimental data that fit Equation 5 may also be described by Equation 1, assuming values of b_0 of zero to -200. The value of the dispersion constant λ_c was in fact proposed as an alternative measure for the helix content of proteins (154). Proteins, such as serum albumin, β -lactoglobulin, and insulin, in the native state give λ_c values in the range of 240 $m\mu$ to 265 $m\mu$. Denaturation is accompanied by a drop in λ_c to 212 to 220 $m\mu$ (154, 200). This behavior however, is not common to all proteins. The dispersion constant of ovalbumin, chymotrypsinogen, ribonuclease, and lysozyme varies little on denaturation (200), while that of rennin, γ -globulin, Bence-Jones proteins, and pepsin rises upon denaturation (120, 121, 122, 180). No satisfactory explanation is as yet available for the "anomalous" behavior of the above listed proteins. It should be remembered, however, that conformations other than the α -helix, as well as amino acid composition and sequence, may markedly affect optical rotatory properties.

It is noteworthy that practically all proteins show a marked increase in their levorotation upon denaturation. Changes in specific rotation, measured at a given wavelength, have thus been adopted as a sensitive tool for the detection of the corresponding alterations in macromolecular conformation. A few representative studies of this type will be given. The variation with temperature of $[\alpha]_D$ of insulin revealed a reversible thermal unfolding at about 70°C. (pH 3.6) (200). The variation in the optical rotation of ovalbumin when denatured with urea, in accord with viscosity and ultraviolet-absorption data, suggested that a rapid irreversible uncoiling of the ovalbumin molecule occurs after a certain degree of denaturation has been exceeded (231). The expansion of the serum albumin molecule at acid pH (pH 4 to 2) is similarly accompanied by a corresponding increase in levorotation (135, 230). In the case of papain it was observed that low concentrations of urea or guanidine, which do not cause any significant change in optical rota-

tion, suffice to inactivate the enzyme reversibly. An irreversible loss in enzymic activity occurred only at a high concentration of the denaturing reagents. Protein unfolding was demonstrated at this concentration by the marked change in optical rotation (114).

Hydrogen-deuterium exchange.—The investigation of the rate of hydrogen-deuterium exchange in low molecular weight peptides and proteins in aqueous solution has indicated that the hydrogen atoms of amide bonds that are involved in internal hydrogen bonding exchange with considerably less speed than those fully exposed to the solvent. Hydrogen-deuterium exchange studies have thus become an important tool in the elucidation of the secondary structure of proteins. The literature dealing with this topic has been reviewed by Linderstrøm-Lang (152, 153), Kauzmann (127), Leach (146), and Scheraga (205). Recently it has been shown that complete hydrogen-deuterium exchange of ribonuclease occurs only above 60°C. (pH 4.8) (207). The existence of a transition temperature at which unfolding of the protein molecule occurs (106) has thus been confirmed. Comparing the near infrared absorption of a fully deuterated sample of ribonuclease with that of a sample deuterated below the transition temperature (60°) indicated that the 20-hydrogen atoms that do not exchange below 60° are involved in peptide $\text{NH} \cdots \text{OC}$ backbone hydrogen bonds (111). Partial unfolding of secondary structure also was found in subtilisin-modified, but still enzymatically active, ribonuclease (172). The number of slowly exchangeable hydrogen atoms of the modified ribonuclease was smaller by 20 than that of the intact enzyme. After separation of the 20-amino-acid peptide, which presumably contains no slowly exchangeable hydrogens, the protein core was found to contain a still smaller number of slowly exchanging hydrogens. Recombination of the protein core with the peptide restored the number of slow hydrogens found before separation. Studies on the hydrogen-deuterium exchange of ribonuclease in LiBr solutions suggested simultaneous folding and unfolding of the molecule (232). In view of these results the explanation presented by Harrington & Schellman (107) that the LiBr causes maximum intramolecular hydrogen-bonding seems oversimplified. For myoglobin, a helix content of about 50 per cent was derived from hydrogen-deuterium exchange data at pH 7.0 (19, 20). This value is in rough agreement with that estimated from the x-ray analysis of the crystalline protein (70 per cent) (130). Loosening in structure occurred at pH 8.8 where the helix content decreased to 38 per cent. Deuterium exchange experiments with chymotrypsinogen indicated that the stability of at least 40 hydrogen bonds of the zymogen is drastically altered when the protein passes from the native to the reversibly denatured state at about pH 2.0, or a temperature of about 50° (261). An infrared absorption study of the hydrogen-deuterium exchange of some fibrous proteins, such as α -keratin, silk-fibroin, and stretched wool, was carried out by Fraser & MacRae (89, 90). In every case replacement of hydrogen by deuterium in the peptide linkage occurred preferentially in the less orientated regions of the specimen.

Berger & Linderstrøm-Lang (23, 153) suggested a general mechanism to explain the kinetics of exchange by deuterium of the hydrogen atoms involved in internal hydrogen bonding. In this mechanism it was assumed that the internally hydrogen-bonded starting material A reversibly forms an intermediate A_1 in which the internal hydrogen bonds are ruptured. The deuterated product A_2 is formed as a result of a reaction between A_1 and a deuterium donor DQ (D_2O , OD^- , or D_2O).



In the case of poly-DL-alanine the exchange reaction proper ($A_1 \rightarrow A_2$) was considered the rate-limiting step of the overall reaction. In the case of insulin, however, the rate determining step was assumed to be that of hydrogen bond rupture ($A \rightarrow A_1$) (152). The conclusion drawn as to the helical conformation of poly-DL-alanine (23) has been questioned recently by Bryan & Nielsen (44). The latter authors observed that the H-D rate of exchange of poly-DL-alanine is considerably faster than that of poly-L-glutamic acid when in helical configuration (69) and is of the same order of magnitude as that found in simple di- and tripeptides (170).

In reviewing the data so far obtained it is worth emphasizing that a slow H-D exchange should by no means be considered proof of the existence of an α -helix configuration. Other hydrogen-bonded polypeptide conformations, as well as the shielding of exchangeable hydrogens by hydrophobic regions, may also reduce the rate of H-D exchange.

The effect of deuterium-hydrogen substitution on bond strength in ribonuclease (110) and poly- γ -benzyl-L-glutamate (47) has been investigated recently. From the change in the helix-coil transition temperatures in the suitable media, it was concluded that the substitution of deuterium for hydrogen favors the helical form in both cases.

Enzymatic examination of secondary structure.—Denatured proteins generally are digested more readily by proteolytic enzymes than by the corresponding native proteins. It might be assumed, therefore, that the random regions of a native protein molecule will be more susceptible to proteolysis than will the helical regions. A kinetic analysis of the enzymatic hydrolysis of a given protein may thus provide important information as to its macromolecular configuration. A kinetic analysis of the tryptic digestion of myosin in a temperature range of 6° to 25° (109, 159) pointed to the existence of two parallel first-order reactions with markedly different velocity constants. Approximately 64 peptide bonds are cleaved in the fast reaction and 240 peptide bonds in the slow reaction. On raising the temperature to 41° a significant fraction of the bonds split in the slow reaction was transferred to the fast reaction. Based on these data, a model was proposed for myosin in which polypeptide chains were arranged parallel to one another, and the segments of high order alternate with segments that are more randomly disposed. The finding that, on short exposure to subtilisin and chymotrypsin,

myosin yields meromyosin-like components (92, 158), similar in their hydrodynamic properties to those formed on partial tryptic digestion seems to support the above model. The hydrolysis of native ichthyocol collagen by collagenase at a temperature below 27° also shows overall kinetics that can be reduced to the sum of two concurrent reactions, both apparently first order in substrate concentration (250). Since conversion to gelatin, above 27°, reduces the kinetics of proteolysis to a single apparent first-order reaction, the complex kinetics observed for the native protein have been interpreted in terms of local differences in polypeptide chain configuration in the vicinity of the susceptible peptide bonds. It is noteworthy that the first stages of collagenolysis are accompanied by a rapid fall in specific viscosity, although no marked change occurs in molecular weight or specific optical rotation. These results were interpreted in terms of a rigid, multistranded, interchain, hydrogen-bonded structure for the collagen macromolecule in solution. Enzymatic cleavage of single strands leaves the particles relatively intact but brings about a partial structural collapse by introducing points of increased flexibility. The formation of a collagen-like structure when ichthyocol gelatin solutions (52, 191) are cooled below 27° was also examined enzymatically (109, 251). From the onset of the complex kinetics of collagenolysis on cooling, as well as from optical rotatory and viscosity data, it was concluded that the gelatin-collagen fold transition takes place in three steps: (a) a rapid, local intrachain configurational change involving the locking of proline residues into the poly-L-proline II configuration (229); (b) development of a loose poly-L-proline II type helix along the gelatin molecules; and (c) close packing that leads to interchain associations. Collagenase is known to split specifically the X-Gly link in the sequence -Pro-X-Gly-Pro-, where X denotes an unspecified amino acid (250). The rate of collagenolysis will therefore be determined by step (a), while the steps (b) and (c) will be reflected by the corresponding changes in optical rotation and viscosity. Finally, it is of interest to note that although collagen and gelatin appear to bind collagenase equally, gelatin is degraded at a rate approximately ten times greater than that for collagen (209).

TERTIARY STRUCTURE

Ultraviolet spectral changes.—The ultraviolet absorption maxima of proteins, in the 250 $m\mu$ to 310 $m\mu$ region, undergo shifts to shorter wavelengths when the secondary and tertiary structures of the molecules are disrupted (15). In the interpretation of this effect, attention has been directed particularly to the tyrosyl side chains because of the possible contribution of phenolic hydroxyl groups to the stability of the tertiary structure of proteins via hydrogen bonding. In 1943 Crammer & Neuberger (59) detected spectrophotometrically that some of the tyrosine hydroxyl groups of native ovalbumin were not free to ionize at pH 12. This was explained by suggesting that the phenolic hydroxyl groups are hydrogen bonded to appropriate acceptors, possibly carboxylate ions, in the adjacent parts of the folded na-

tive protein molecule. The finding that the number of abnormally strong carboxyl groups in ovalbumin equals that of the abnormally weak phenolic groups (105) can be taken as supporting evidence for the above hypothesis. Spectrophotometric data indicating the existence of hydrogen-bonded tyrosyl groups have also been obtained for other proteins (26, 143, 145, 203, 210).

The spectral changes accompanying denaturation, acidification, or hydrolysis of proteins may be accurately measured by means of an ultraviolet difference spectrum technique, in which the optical density of the treated protein is compared with that of the intact material (145). Some of the new results obtained by this method will be given below. The appearance of difference absorption peaks at 279 $m\mu$ and 287 $m\mu$ on tryptic digestion or acidification of insulin indicated the breaking of tyrosyl hydrogen bonds (143, 145, 147). From the amino acid sequence of insulin and the information available as to the bonds split by trypsin, it was possible to specify the two tyrosine residues of the B chain (B26 and B16) that participate in the tertiary structure. The presence of hydrogen-bonded tyrosines also was demonstrated in ribonuclease. An abnormal ionization behavior of three of the six tyrosine residues (222, 237) and of an indeterminate number of carboxyl groups (236) was deduced from titrations. "Normalization" of the electrochemical behavior of these groups occurred on denaturation (36, 48). The ultraviolet difference spectra obtained at acid pH, before and after pepsin inactivation, revealed that only one of the three abnormal tyrosines of ribonuclease is hydrogen bonded to a carboxylate ion (25, 26). It is of interest that the configurational changes in ribonuclease that occur on heating or acidification lead to a simultaneous change in optical rotation and ultraviolet absorption spectrum (111). Spectral studies have indicated that the molecular unfolding of ribonuclease induced by urea or guanidine hydrochloride may be prevented by polyvalent anions and polyanions (211). Characteristic changes in the ultraviolet absorption, in the range of 250 $m\mu$ to 310 $m\mu$, were also observed on the denaturation of chymotrypsinogen (50), on acidification of L-meromyosin to pH 2 (233), and during the autolysis of pepsin (37) and trypsin (225).

Difference spectra similar to those observed in proteins when the pH is displaced from neutrality to acid values near 2, were obtained with O-methyltyrosine in concentrated sodium acetate or in urea solutions (259). Since O-methyltyrosine cannot form the type of tyrosyl hydrogen bonds attributed to proteins, it could be concluded that the difference spectra in proteins may result not only from the rupture of such bonds but also from changes in vicinal electrostatic charges, as well as from alterations in the polarity and polarizability of the environment of the chromophoric groups. Indeed, the short wavelength shifts in the phenylalanyl, tryptophyl, and tyrosyl absorption regions, observed when proteins are structurally modified, are closely parallel to changes in the spectra of benzene, indole, and phenol, respectively, on passing from solvents of higher to lower refractive index (40, 264).

The different factors that may affect the ultraviolet spectra of proteins have been discussed recently by Leach & Scheraga (148). In accord with the above, it was found that the pH dependence of the differential spectrum of anthracene coupled to bovine plasma albumin can be explained only by a configurational alteration in the molecular structure (263). Changes in the ultraviolet spectrum of bovine albumin, in a pH range of 2 to 4, could be similarly explained (262). In conclusion it should be stated that changes in the ultraviolet spectra may reflect slight alterations in tertiary structure. Extreme caution, however, must be exercised in the interpretation of spectral shifts in terms of changes in protein structure.

Hydrophobic bonds.—By the term hydrophobic bonding it is customary to denote the tendency of the non-polar groups of proteins to adhere to one another in aqueous environments. The important role of the hydrophobic bonds in stabilizing the folded configuration in native proteins has been discussed recently by Kauzmann (128). In his review, Kauzmann (128) pointed out that the most appropriate model systems for the study of the thermodynamics of the hydrophobic bond are aqueous solutions of hydrocarbons and other small organic molecules containing non-polar groups (85). From such studies it was estimated that the free energy change in the transfer of non-polar side chains such as those of leucine, valine, and phenylalanine from water to a non-polar environment is exergonic to the extent of about 3000 to 5000 cal. per mole of groups at room temperature. This stabilization of the hydrophobic bonding is largely attributable to entropy effects since water-molecules in the immediate vicinity of non-polar groups seem to arrange themselves into a quasi-crystalline structure in which there is less randomness than in ordinary liquid water (85). The elimination of the hydrophobic stabilizing effect in non-aqueous solvents such as ethanol, or at high concentrations of detergents, explains the denaturation of proteins by these agents. Hydrophobic bonding also might be involved in protein aggregation and binding reactions. Such reactions are frequently accompanied by small enthalpy changes and large entropy changes.

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